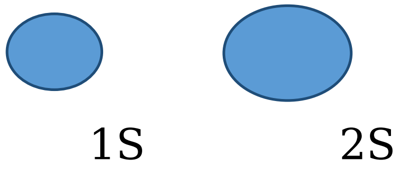
An introduction to physical organic chemistry

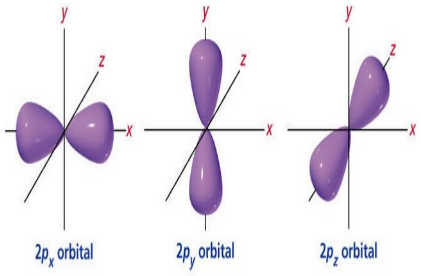
Atomic orbital

The atomic orbital is simply the region in space where an electron is likely to be found. These orbitals have different kinds and different size depending upon the energy of the electrons.

The orbital can be pictured as cloud of negative charge which is not uniform but is densest in the regions where the probability of finding the electrons is high.

The orbital at lowest energy level **(1S)** is spherical in shape with the nucleus of atom at its center at the next higher level there is the spherical **(2S)** orbital and three perpendicular dumb bell shaped **2P** orbital namely **$2P_x$,$2P_Y$,$2P_Z$**





Each orbital can accommodate only 2 electrons with opposite spinning (paul exclusion)

An orbital becomes occupied after the orbitals of lower energy are filled.

According to Hunds rule: an orbitals is not occupied by a pair of electrons until other energetically equivalent orbitals degenerated orbitals.

2P orbitals are each occupied by one electron.

Thus hydrogen atom has one electron only in the 1S orbital and the electronic configuration of the carbon atom in the ground state will thus be $\mathbf{IS^2,2S^2,\ 2P^1x,\ 2P^1y}$

Where the remaining $\mathbf{2P_z}$ orbital is empty.

It would appear that carbon is bivalent only two unpaired electrons are available for bond formation with other atoms .however, carbon exhibits quadrivalency in its compounds.

This can be achieved by (promoting) one of **2S** electrons to the vacant 2P orbital.

The carbon atom now become in the higher state (exited): $\mathbf{IS^2,2S^1,\ 2P^1x,\ 2P^1y,\ 2P^1{}_z}$

Now four unpaired electrons are available to form bonds with other atoms or groups.

Hybridization

When carbon atoms is attached to four other atoms we must might expect it.to form three bonds of one kind (using the **2P** orbital) and one bond of another kind (using the **2S** orbital), in fact, the four bonds are exactly equivalent in energy, and lying at equal angles to each other $109^0\ 28^\backslash$ and are directed to the corner of tetrahedron.

This can be accounted for by hybridization of the **2S** and the three **2P**atomic orbital so as to yield four new identical orbitals which are capable of forming stronger bonds.

These are known as **SP^3** hybrid atomic orbitals and this process called (**SP^3Hybridization**)

When the carbon atom is combined with three other atoms only in ethylene **C_2H_4** another redeployment is envisaged by hybridization where the **2S** and only two of the **2P** orbitals are combined to form three new hybrid orbitals, disposed at 120 to each other in the same plane (**SP^2** plane trigonal hybridization) leaving one unhybridized**2P** atomic orbital at right angles to this plane.

The three hybrid orbitals are used to form strong sigma **(б)** bonds by overlapping in this case with **1S** orbitals of the two hydrogen atoms and **SP^2** hybrid orbital of the other carbon atom.

The unhybridized **2P** orbitals on the two carbon atoms are parallel and overlapped laterally forming a weaker **(π)** bond.

In acetylenic compounds, carbon atom forms two sigma bonds by two hybrid orbitals derived from the **2S** orbital and one only of the **2P** atomic orbitals resulting in linear molecule with two unhybridized 2P atomic orbitals lying at right angles to each other carbon atom.

The parallel **P** orbitals overlap laterally to form the two **(π)** bonds in planes at right angles to each other.

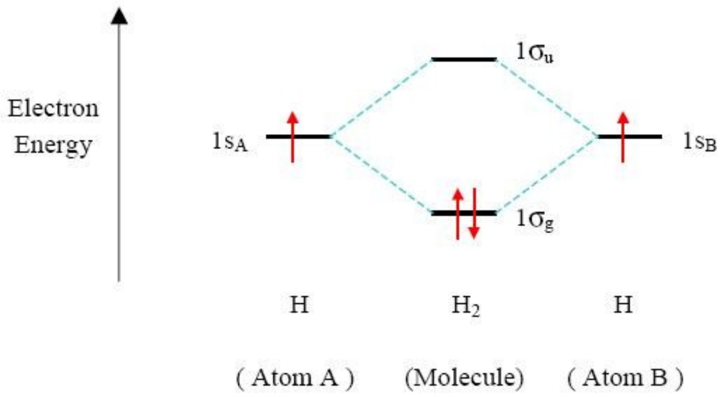
It will be seen that hybridization takes place so as to permit stronger bond formation.

The greater the possible overlapping of the atomic orbitals.

The stronger the bond so formed.

The two overlapped atomic orbitals are the replaced by the two molecular orbitals spreading over both atoms .

1. Bonding **(sigma)** molecular orbital having less energy than the two separate atomic orbitals in which the two electrons tend to be concentrated to form stable bond.
2. Antibonding **(sigma*)** molecular orbital having more than the energies of the two separate atomic orbitals, this orbitals remain empty in the ground state of the molecule and have no role in stable bond formation.



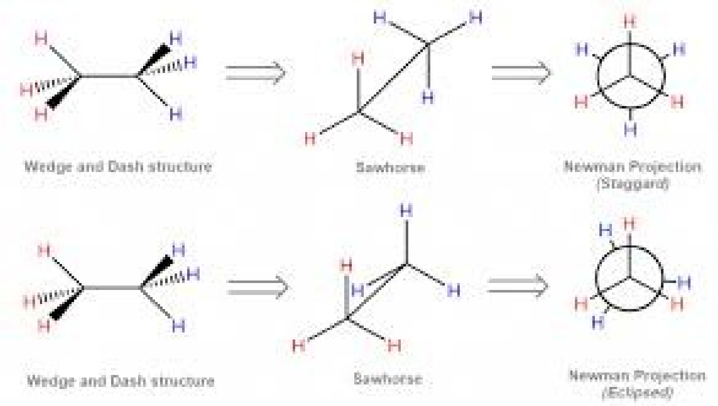
Strong **(sigma)** bond formation needs the atomic orbitals to be overlapped axially along their major axis.

This sigma bond joining the two carbon atoms (e.g. ethane) is symmetrically about a line joining the two nuclei .and permits free rotation about it.

Thus ethane molecule can take an infinite variety of different structures according to the relation position of the hydrogens on other carbon atoms with respect to each other.

These are known as different conformations (different arrangements of the same group of atoms that can be converted into one another without the breaking or forming of any bonds.

The two extremes of all are known as the eclipsed and staggered forms as shown in the following projections.



The staggered conformation is more stable since the hydrogen atoms on the adjacent carbons are as far apart from each other as possible, and thus the non – bonding interaction between them is at minimum.

The eclipsed conformation is suffers from maximum crowding which display more effects especially in presence of substituents of large size.

The situation is different in a case of unsaturated carbon compounds where free rotation around double or triple bonds is restricted.

Stability of Alkenes

Available information about relative stability of alkenes can be provided in terms of heats of hydrogenation and combustion.

Heat of hydrogenation

It is the quantity of heat evolved when one mole of the unsaturated compound is hydrogenated into the saturated one.

While heat of combustion

Is the quantity heat evolved when one mole of hydrocarbon is burned into carbon dioxide and water?

Heats of hydrogenations for alkenes having similar structure are remarkably constant for compounds containing more than one double bond we might expect a heat of hydrogenation equal to the sum of the heats of hydrogenation of the individual double bonds which is only found to be hold for non- conjugated system.

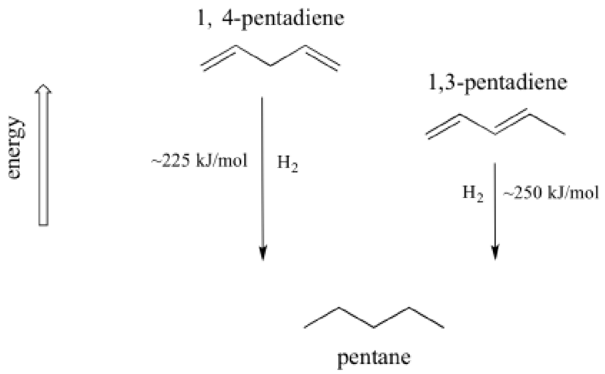
In conjugated system, however, the measured values are usually slightly lower than expected e.g. heat of hydrogenation of the non-conjugated 1, 4 pentadiene

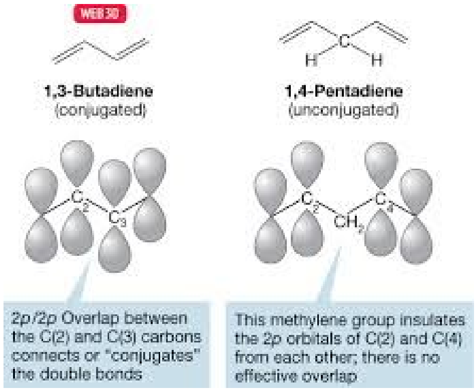
$CH_2=CH-CH_2-CH=CH_2$ is equal to 61 kcal/mole as expected.

While that for the conjugated 1, 3 pentadiene

$CH_2=CH-CH=CH-CH_3$ is equal to 54kcal/mole.

They both consumed two mole of hydrogen and yield n- pentane





2p/2p Overlap between the C(2) and C(3) carbons connects or "conjugates" the double bonds

This methylene group insulates the 2p orbitals of C(2) and C(4) from each other; there is no effective overlap

This means that 1, 3 pentadiene contains less energy, more stable than the non-conjugated 1, 4 pentadiene.

Taking the heat of combustion into consideration similar result were obtained.

In 1, 4 pentadiene ,lateral overlap of **P** atomic orbitals on adjacent carbon atom leads to the formation of two localized (π) bonds.

While in the 1, 3 pentadiene ,lateral overlap could take place between all four **P** atomic orbitals on adjacent carbon atoms leading to the formation of 4 **(π)** molecular orbitals.

Two bonding and two antibonding .

In the latter case, accommodation of the 4 electrons in the bonding molecular orbitals results in 4 conjugated carbons.

The electrons are said to be delocalized and held in common by the whole conjugated system.

Delocalization is much involved in lowering the total energy of the conjugated system in both of its ground and exited state.

This explain why the conjugated system undergoes more readily addition reaction than does an isolated one.

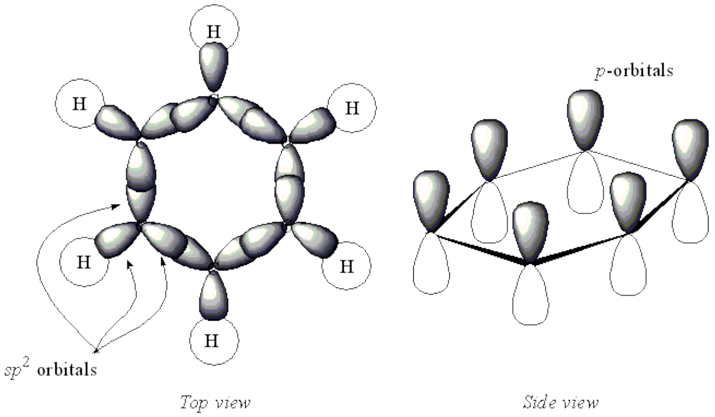
The four **P** atomic orbitals in 1, 3 pentadiene would have to be essentially parallel to permit such delocalization resulting in a considerable restricted rotation about the **C2-C3** bond which has now some double bond character.

Benzene and Aromaticity

The currently accepted picture of benzene molecule arises from an extension a modification of old structural theory.

The cyclic planar regular hexagonal structure implies **SP^2** hybridization with **P** orbitals at right angles to the plane of the molecule on each of the six carbon atoms.

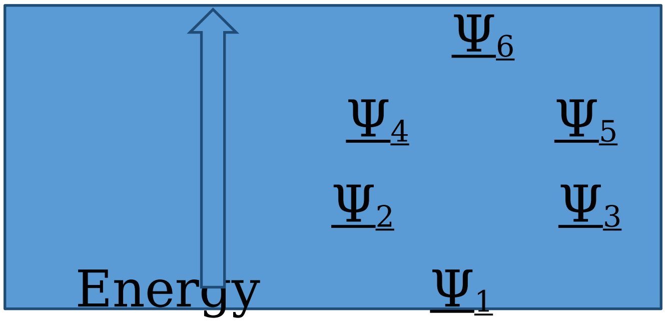
The carbon- carbon bond length in benzene are exactly the same **(1.4A)** somewhere in between the normal values of single bond **(1.54A)** and double bond **(1.33A).**



Overlapping could occur between **P** orbitals associated with carbon atoms 1:2,3:4,5:6 and with the same probability between those on carbon on atoms 1:6,5:4,3:2 the net result is simultaneous overlapping between all six adjacent **P** orbitals.

This results in the formation of six molecular orbitals three bonding **(Ψ_1-Ψ_3)**

And three antibonding **(Ψ_4-Ψ_6)** each bonding molecular orbital cannot accommodate more than two electrons.



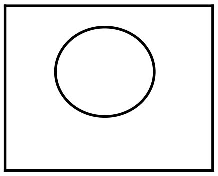
Degenerate orbitals (M.O of benzene)

The molecular orbital 1 of the lowest energy is cyclic embracing the six carbon atoms with nodal plane of the ring.

The other two degenerate molecular orbitals 2 and 3 are of equal energy and also encompass all the carbon atoms, with further nodal at right angles to the plane of the ring as shown above (the upper view of each orbital is shown).

The net result is an annular electron cloud above and below the plane of the ring.

The old kekule structures of benzene are clearlyinadequate, instead, the best representation can be written as follow:



The remarkable thermodynamic stability of benzene can thus be attributed to the plane trigonal sigma bonds about each carbon at their optimum angle of 120˚

And to the cyclic delocalized molecular orbitals that accommodate the six **(π)** electrons.

Benzene is thermodynamically more stable than hypothetical (cyclo-hexatriene) system (kekule structure) by 36 kcal/mole which referred to as delocalization energy.

The term “resonance energy” through still widely used is not quite correct as it may means a rapid oscillation between different structures.

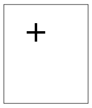
Hukels rule for aromaticity

Aromatic stability (high delocalization energy) is associated with systems having **(4n+2)π** electrons in closed shell, whatever the number of carbon atoms where n is an integer can take the values **(0, 1.2, 3…).**

Some ionic species which fulfill this condition show quasi-aromatic strucures are also known e.g.:

Cyclopropenyl cation(1)which have **2π** electron (**n=0**),cyclopentadienyl anion(2)

And cycloheptatrienyl cation (3) (tropylium) both have **6π** electrons (**n=1**)as well as benzene and pyridine.



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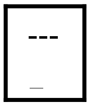

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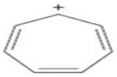
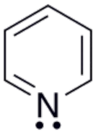


Cycloheptatrienyl cation

3

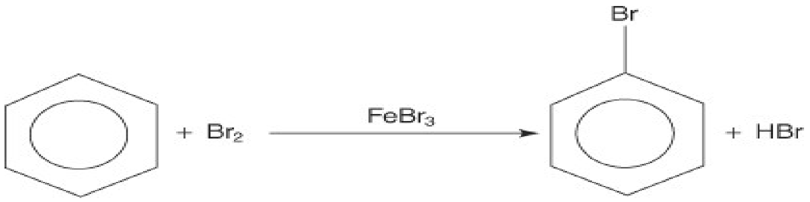


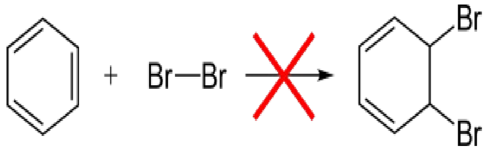
Naphthalene is an example for **10 π** electrons system **(n=2)** and antharacene and phenanthren are example for **14 π** electrons system **(n=3)**.

The requirements necessary for aromaticity can thus be summarized into:

- The molecule should be flat to permit cyclic lateral overlap of **P** orbitals.
- The bonding orbitals should be completely filled with **(4n+2)π** electrons.

The stability attained by delocalization in aromatic systems explained why their characteristic reactions are mostly substitution rather than additional once as might expected, since addition reaction would lead to decrease in the number of delocalized orbitals and the cyclic overlap is then not allowed,while substitution reaction will not disturb the delocalization of the cyclic system.





Polarity of covalent bonds and dipole moment

The covalent bond between two atoms involves a sharing of two electrons one from each atom, besides their spins must be anti-parallel.

When covalent bond is formed between two identical atom ,e.g.

H-H, C-C … etc.

The two electrons forming it are symmetrically disposed between the two atoms. Therefore, the centers of gravity of the electrons and nuclei coincide in the molecule. But when the two atoms are not similar, the covalent bond electrons are somewhat displaced towards the more electronegative atom. The bond become polarized.

$H \rightarrow F$ or $H^{+}-F^{-}$ & $H^{\delta+}\text{-}O^{\delta-}\text{-}H^{\delta+}$ & H-N-H

Such molecule constitute a dipole and symbolized by → where the arrow points to the electronegative atom.

The molecule possesses a dipole moment **(μ)** which is equal to the magnitude of the charge **(e)** multiplied by the distance **(d)** between the two charged centers.

$$\mu = e * d$$

The polarity of a molecule depends not only up on the polarity of its individual bonds but also upon the way in which the bonds are directed in space, upon the shape of the molecule.

For example tetrachloride have	μ	carbon zero D unit

Therefore dipole moment measurements give valuable information about structure of the molecules.

Hydrogen bonding :association and chelation.

Among molecules which are held together mainly by Vander wall forces, e.g.: hydrocarbon the main factors that determine boiling and melting points are the molecular weights and shapes of molecules.

In general within a family of the periodic table a decrease in molecular weight accompanied by a decrease in boiling and melting points.

However, when we examine the boiling points of hydrogen compounds for some groups in the periodic table, we find some exception to this rule as in a case **HF,H_2O,NH_3**.we might expect that **HF** has the lowest boiling point of its group ,but it has by far the highest one (the boiling points decrease as we proceed from **HI** to

HBr to **HCl**) in the next two families there are similar jumps in b.ps of **H_2O** and **NH_3**.

These abnormalities can be attributed to the presence of hydrogen bonding

H…F…H…F…H

Hydrogen bonding is simply as especially kind of dipole- dipole attraction.

It is an electrostatic in nature and is about 5-10% as strong as most covalent bonds.it is usually represented by dotted line.

Usually ,hydrogen bonding is available only when hydrogen is attached to a highly electronegative atom, where it acquires afractional positive charge and the other atom acquires an equivalent negative charge to degree enough to perform the necessary attraction.

In this situation the hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and other by purely electrostatic forces.

Hydrogen bonding may classified into:

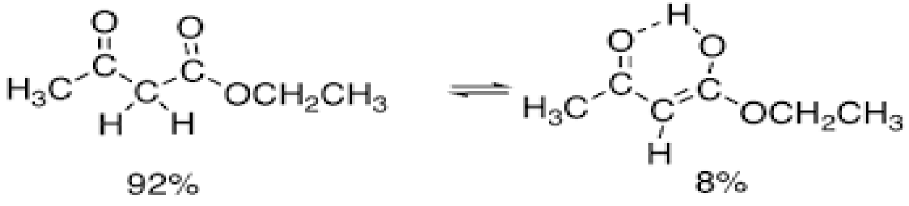
A. Intermolecular hydrogen bonds:

It is present between two molecules and causes what is known as associated phenomena,**HF,H_2O,NH_3** are examples of associated compounds and this is the reason for their relatively high melting points as an extra energy is required to break such hydrogen bonds. Like water, alcohols are associated compounds with abnormal high boiling points.

The solubility of the lower alcohols in water is due to mainly to the hydrogen bonding that can exist between alcohols, phenols and water, there is no obvious limit to the total number of molecules that can associated through hydrogen bonding.

B. Intramolecular hydrogen bond.

It is exist within the same molecule resulting in what is known as chelation phenomena e.g. The enol form of ethyl acetoacetate.



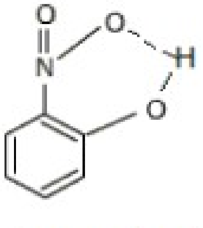
Ethyl Acetoacetate
(a β-ketoester)

In this type of bonding molecules are unassociated and generally have lower boiling and melting points than the comparable ones with intermolecular hydrogen bonding.

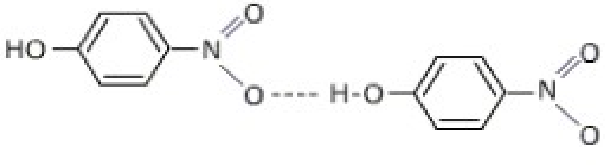
Intramolecular hydrogen bonding take place also when the formation of 5,6 or 7 membered ring is possible.

On comparing some benzene derivatives such as o-,m-,p-nitrophenol,we find than only o-derivative can present in chelate structure due to the presence of intramolecular hydrogen bonding resulting in aconstant low volatility and low solubility in polar solvents.

On other hands, the **m-,p- derivatives** have comparatively high points due to the association resulting from inter molecular hydrogen bonding with solvent molecule.

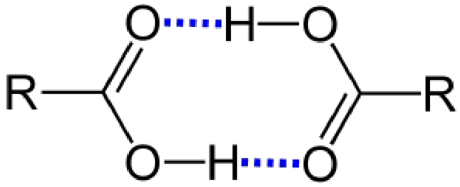


Inter molecular hydrogen bonding



Intra molecular hydrogen bonding

Carboxylic acids possess an **(OH)** group permitting intermolecular hydrogen bonding however it is restricted to only a pair of molecules.



O-hydroxybenzoic acid (salicylic acid) strength is considerably greater than that of m- or p- isomers as a result of intra molecular hydrogen bonding which stabilizes its anion by delocalization its charge an advantage not shared by the other isomers.

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The breaking and forming of covalent bonds :

The chemical reaction usually involves the breaking or forming chemical bonds Covalent bond can be broken either :

- Homolytically : each atom acquire one electron
  $\mathbf{X-Y \rightarrow \dot{X} + \dot{Y}}$
  This results in the formation of free radicals (F.R)which are highly reactive the opposite type of such reaction is known as coilication and such mechanism is known as F.R . Mechanism.
- Heterolytically: in which one atom only acquires the two electrons.
  $\mathbf{X{:}Y \rightarrow X{:}^{-} + Y^{+}}$

Or $\mathbf{X{:}Y \rightarrow Y{:}^{-} + X^{+}}$

And this results in the formation of positive and negative ions.

The backward reaction is known as coordination and such mechanism is known as ionic mechanism.

Positively charged carbon atom is known as carbonium ion and negatively charged carbon atom known as carbanion.

Some characters which can help to differentiate between the ionic and F.R mechanism:

The ionic reactions rarely occur in the vapor phase and are affected by polar solvents and usually catalyzed by acids and bases.

F.R reaction proceed readily in vapor phase and in non-polar solvents catalyzed by light or **U.V** radiations and inhibited by compounds such as hydroquinone or diphehyl amine which known as acceptor

F.R reaction are auto- catalytic and follow a chain reaction while reactions usually follow uni molecular or bimolecular mechanism.

Factors affecting distribution and mobility of electrons in bonds and individual atoms.

The physical properties as well as the chemical reactivates of organic molecules are depend upon a number of factors that influence the relative availability of electrons in particular bonds or at particular atoms.

A number of such factors have been recognized:

1. Inductive effect (polarization effect)
2. Inductomeric effect
3. Resonance effect (mesmeric effect)
4. Electromeric effect

5. Hyper conjugative effect (hyper conjugation)

The inductive effect

In a covalent single bond between unlike atoms the electron pair forming the bond is never shared absolutely equally between the two atoms since it tends to be attached a little more towards the more electronegative atoms.

Thus in an alkyl halide (alkyl chloride) **R-Cl** the electron density tends to be greater nearer chloride than carbon as former is the more electronegative.

This inductive displacement represents a permanent polarization in the molecule.

And is generally represented in a classical formula by $\mathbf{R^{+}\text{-}CL^{-}}$ **or** $\mathbf{R \rightarrow CL}$**.**

If the carbon atom bonded to chloride is it attached to carbon atoms the effect can be transmitted further although it becomes weaker as we go down the chain from $\mathbf{C_1}$ **to** $\mathbf{C_4}$.

C-C→C˃˃C˃˃˃CL

The inductive effect is always symbolized as **(+I or –I)** it is taken as as **(-I)** if the atom or group is more electronegative (is more attracting electrons) and **(+I)** if atom or group is more electron donating than hydrogen

R→X (-I) **R←X (+I)**

Some of the important feature of the permeant inductive effect are:

- The electron displacement occurs from carbon without the transference of any electrons from the octate of one atom to another.
- The changes produced by such displacement are all in one direction.
- The effect decrease gradually as it passes away from the atom or group inducing it.

Inductive effect and strength of organic acid:

As an illustration of the influence of the inductive effect on properties of organic compounds we are going to have a look at the strength of group of carboxylic acid.

The ionization of carboxylic acid in water solution expressed by the equation:

$$\mathbf{RCOOH + H_2O \rightleftharpoons RCOO^{-} + H_3O^{+}}$$

This involve attack by the water molecule on the hydrogen atom of carbonyl

Any effect within the carboxylic acid molecule tending to decrease the electron density on the acidic hydrogen should facilitate the ionization .that is, if substituent attracts electrons **(-I effect)** the proton will be held less firmly in carboxylic group and acidic strength will be increased.

If the substituent is electron releasing relative to hydrogen (+I effect), the resulting increase in electron density in carboxylic group will held the proton more strongly and acidic strength will be decreased.The above facts as well as the fact that the inductive rapidly dies out as it is transmitted down a saturated chain is clearly shown by the data represented in the following table:

Acid	**K_A**	**Acid**	**K_A**
Formic	**$1.77*10^{-4}$**	**(x -chloro**	**$3*10^{-5}$**

		Butyric)	
Acetic	$1.74*10^{-5}$	Fluroacetic acid	$2.1*10^{-3}$
Propanoic	$1.34*10^{-5}$	Bromoacetic acid	$1.3*10^{-3}$
n-Butyric	$1.51*10^{-5}$	Iodoacetic acid	$7.1*10^{-4}$
iso-Butyric	$1.4*10^{-5}$	Methoxy acetic acid	3.3*10-4
Chloroacetic	$1.4*10^{-3}$	Cyanoacetic acid	$4*10^{-3}$
di Chloroacetic	$5*10^{-2}$	Vinylacetic	$3.8*10^{-5}$
tri Chloroacetic	$1.3*10^{-1}$	Benzoic acid	$6.5*10^{-5}$
α-chloro Butyric	$1.5*10^{-3}$	Phenylacetic acid	$6.5*10^{-5}$
β-chloro Butyric	$8.8*10^{-5}$		

From the above table it is clear that there are considerable differences between the strength of some of acids listed. Formic acid is a little stronger acid than acetic acid because the hydrogen atom attached to the carboxyl group is considered to be more electron attracting than the methyl group in a case of acetic acid.

The high acid strength of Chloroacetic compared with acetic acid resulting from the electron attracting power of (-I effect) the substituent halogen relative to carbon to which it attached.

The electron attracting power of three such halogen atom is of course expected to be greater than that of one halogen. Hence tri Chloroacetic acid ($1.3*10^{-1}$) is remarkedly a stronger acid than Chloroacetic ($1.4*10^{-3}$).

As would be expected from the explanation of inductive effect its influence on **K_A** falls rapidly with increasing distance of the substituent from carboxyl group .this is readily seen by the significant difference between the K_A values of the **α, β** and **ɤ -chloro Butyric**.

Other groups besides halogens are electron - withdrawing (-I effect).among these are nitro

NO_2, methoxy **CH_3O^-**, carbonyl **(C=O)** as aldehydes, ketones, acids, esters and amides **(-CN)**, trialkylammonium **(R_3N^+)** and amine group (-**NH_2,NR_2).**

Alkyl groups, methyl, ethyl, isopropyl are only substituents which are electron releasing and hence they are acid weakening relative to hydrogen.

The magnitude of their electron releasing effect does not appear to change greatly ongoing from methyl to propyl.

The inductive effect is general phenomenon and plays an important role in the distribution of electrons charge in molecules .we shall have occasion later to observe its operation in variety of molecules.

2- The inductomeric effect

The inductive effect considered above is a permanent effect existing in the non-reacting molecules .during reactions by a polar mechanism, however a molecule is under the direct influence of an electric field created by the attacking reagent ,and it is to be expected that the normal electron distribution within the molecule could be distributed by this field ,thus in addition to the permanent inductive effect which may we may call the inductomeric effect will depend on the nature of attacking reagent and its closeness to attacked molecule whereas the permanent inductive effect may either aid or hinder a given reaction depending upon its direction and magnitude, the inductomeric effect can only aid reaction ,it could not possibly hinder a reaction.

Inductomeric effect and the comparative reactivity of alkyl halides:

We may illustrate the use of inductomeric effects through consideration of the relative reactivity of **RF, RCL.RBr**, and RI in their reaction with hydroxide ion to give the corresponding alcohol

$\mathbf{R{-}{-}{-}{-}X+OH^{-}\rightarrow ROH+X^{-}}$

In this reaction the negatively charged hydroxide ion attacks the partially positive carbon atom attached to halogen, thus the success of this attack depends upon the degree of positive charge on carbon atom.

It is found that for a given **R** group, **RI** compounds are the most reactive and **RF** are the least ,the bromides and chlorides are intermediate and the order of decreasing reactivity is

RI˃RBr˃RCL˃RF

These experimental results seems unusual when we consider that the inductive or permanent polarization or ionic character of the **C-X** bond increase in the series

C-I˂C-Br˂C-CL˂C-F.

In other words the **C-F** bond is most ionic and **C-I** is the least. So it would seem logical that the carbon atom of the more ionic **C-F** bond will be more reactive than the carbon atom of the least ionic **C-I** bond.

The answer to this puzzle is lies in the property of bonds and atoms we termed previously the polarizability accordingly ,bonds that are pure covalent may be polarized by the application of an electric field or by the approach of an ionic or other charged particle, also bonds having permanent polarization due to an inductive effect may be further polarized by these external influences .the sensitivity of an atom or bond to temporary polarization in this manner is said to be the polarizability of the atom or bond.

This is illustrated by the **C-Cl** bond, which has a degree of partial ionic character indicated by **C-Cl**

If negatively charged ion like $\mathbf{OH^-}$ now approaches the carbon atom along the

C-Cl axis the electron pair of the **C-Cl** bond would be repelled and would move closer to chlorine.

This would results as shown in a greater polarization of the **C-Cl** bond than it had before the approach of the **OH**$^-$ ion.

In order to understand the differing polarization of different bonds, it is necessary to consider the structures of atoms joined by the bond. The outer electron shell of all halogen atoms is held by the nuclear charge in the small fluorine atom, the valence shell electrons are held tightly by the nuclear charge and an external electrical field does not bring about a distortion of electron distribution in valence shell.in an iodine atom, on the other hand, the valence shell electrons are rather far removed from the controlling of nuclear charge and an external electrical field.

Will easily distort the electron cloud of the valence shell as well as the shells nearer the nucleus.

It is general rule that the polarization of the elements of a given family increases with the atomic weight.

The formation of bond between carbon for example, and a highly polarizable atom like iodine gives rise to a bond that is also highly

polarizable. Which means that atoms carry over into the bonds they form with other atoms their characteristic relative polarizabilities.
Returning to the problem of differences in relatives of various alkyl halides .it is seen that differences in polarizability of the **C-X** bond can account for observed difference in reactivity, so, it is now expected that alkyl iodides should be the most reactive since according to the above discussion the order of decreasing polarizability of the carbon-halogen bond is:

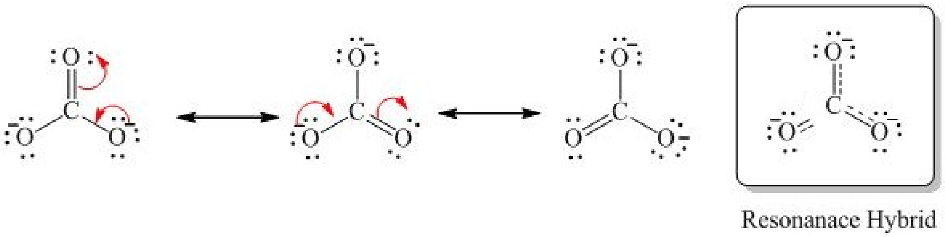
C-I˃C-Br˃C-Cl˃C-F

3 Resonance effect or mesomeric effect

Resonance effect represents essentially another type of electronic displacement

That can take place in unsaturated and essentially in conjugated compounds via their orbitals.

Our structural formula s of such compounds are at best only a rough picture of the true situation in the molecule. And it is not always possible to describe all we known about a given molecule by means of a single picture. An example is the carbonate ion for which we may write the three equivalent structures 1, 2 and 3:



These structures are obtained by changing the positions of the electrons around the oxygen atom with no charge in the positions of the atoms themselves.

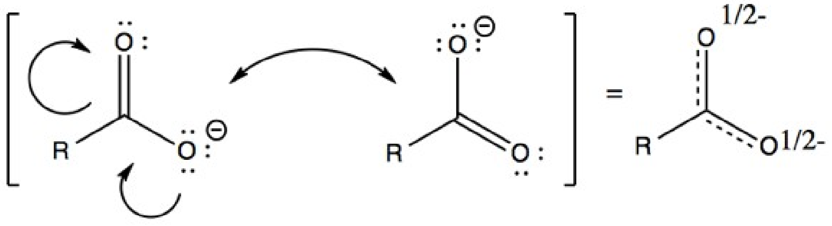
The structures (1), (2) and (3) are called resonating structures or contributing structure of the carbonate ion. Whose properties are not entirly satisfactory represented by any of them.

The actual structure of carbonate ion is more exactly described as a combination of the three a resonance hybrid (4) this was shown as to be true since X-ray analysis of crystalline carbonate ion show that:

a) All three oxygen atoms are equidistant from the carbon atom and from one another, and lie in one plane with carbon atom. Planar configuration is necessary condition for resonance for change of one nonplanar from another would require movement of atoms and not merely redistribution of electrons.
b) X-ray data also established the important fact that in this symmetrical system the interatomic distances are distinctly smaller than would be expected for an average of one double bond and two single bonds.

The distance between the atomic center of the carbon atom and any one of the oxygen atoms of carbonate ion is **1.1A°** whereas in non-resonating system the interatomic distance corresponding to **C-O** bond is **1.43A°** and double bond distance in the normal **C=O** linkage is **1.28 A°.**shortened bond distance are characteristic result of resonance.in resonating molecule bonding energy of the atoms is increased. The atoms are brought closer together and loss of energy resonance confers stability.

The same feature is true with respect to the carboxylate ion which can be written in two forms (5) and (6)



(5) (6) (7).

Physical evidence and theoretical consideration also show that neither (5) nor (6)

Can be considered as a true a picture of the acid ion structure but it is more exactly described as combination of the two as in (7).

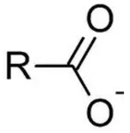
This phenomenon, where two or more electric structures can be written for a given molecule or ion in which only the positions of the electrons differs as shown in the cases of carboxylate ions is called resonance.

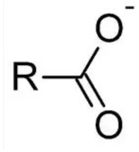
Note that the resonating structures are always joined by a double headed arrow(↔) and it does not means the existence of an equilibrium.

Rules of resonance

In the development of resonance theory there has gradually accumulated no rules with which it is possible to decide which of the alternative written structures should be considered as making contribution to the resulting resonance hydride, these rules can be summarized as follows

1. Only structures which correspond to the same structural arrangement of nuclei may contribute to the state of resonance, which means that the two or more structures contributing to a state of resonance must be inter convertible through a change in the positions of electrons only.
2. Resonance cannot occur between structures containing a different number of unpaired electrons. The significance of the term paired and unpaired electrons has been discussed eailer, for example , in the case of carboxylate ion we have written the two equivalent structures:

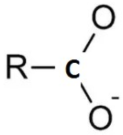




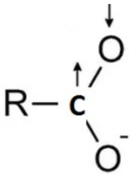
(5) (6)

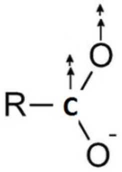
(5) and (6) in which each atom is associated with even number of electrons and all of three electrons are paired either in the atomic or molecular orbitals .We might also write structures for the carboxylate by asymmetrical

cleavage of one of the covalent linkages of the double bond between carbon and oxygen .



The odd electrons on carbon oxygen atoms might on first through be paired as in structure (8) or unpaired as in structure (9)

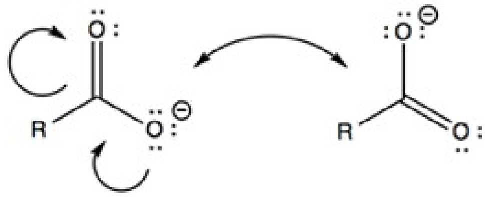


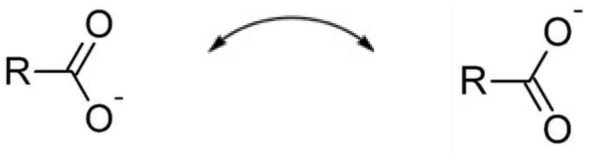


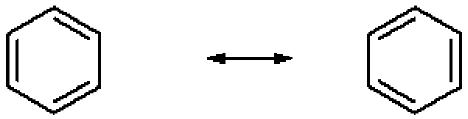
The condition for resonance under discussion state that: there cannot be resonance between structure (6),(7) or(8) of carboxylate ion and structure (9) since structures (9) contains a different number of unpaired electrons.

3. The resonating structures for a given system might not contribute equally to the resonance hydride.

The importance of the contribution of any one structure to the resonance state of the system is determined by the relative stability of that structure, in other words, resonance is of importance only when the structures involved are approximately the same energy.







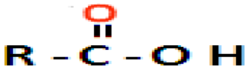
The following points can help in comparing relative stabilities of resonating structures:

a) Structures with the largest numbers of covalent bonds is the most stable.

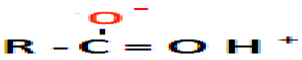
b) Structures which associated more than two electrons with hydrogen or more than eight electrons with any atom of the first row of periodic table are unstable and need not to be considered.

c) Covalent structures involving a separation of charge are general less stable than those not involving a charge separation thus the structure

Is more stable than



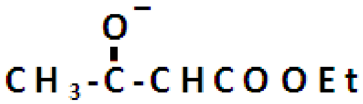
$R-\overset{\overset{O}{\|}}{C}-OH$



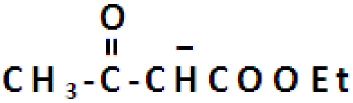
$R-\overset{O^-}{\overset{|}{C}}=OH^+$

and so contributes more to resonance state of carboxylic acids.

d) A structure which carries a negative charge on the atom of highest electronegativity is more stable .thus if we compare the following structures for acetoacetic ester anion we may conclude that the



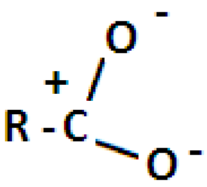
$CH_3-\overset{O^-}{\overset{|}{C}}-CHCOOEt$

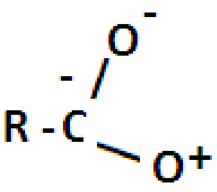


$CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{C}HCOOEt$

Second structure carrying the negative charge on oxygen is more stable than the first one with the negative charge on carbon.

e) Structures with unlike charges placed on adjacent atoms are more stable than structures with like charges placed on the same atom.





Properties of resonating molecules

Molecules exhibiting resonance have certain distinguishing a characteristic which are:

a) The chemical properties of the resonating system may be expected from one or more of the contributing structures, or it could be intermediate in character.

b) Resonating molecules are of lower energy content, more stable than non –resonating molecules having the same bond types. Consider for example the case of benzene were it is more stable than what we might call classical or non-resonating 1,3,5 cyclohexatriene.the heat liberated in burning one mole of benzene into carbon dioxide and water is estimated by considering benzene as six **C-H** bonds three **C-C** single bonds and three **C=C** double bonds ,however, the experimental heat of combustion of benzene is 36kcal/mole lower than the theoretical value calculated from bond energies. Thus benzene is stabilized by resonance and has a resonance energy of 36kcal/mole so the resonance energy is difference between the actual energy content of a resonating molecule and the calculated energy content of by adding up the bond energy values in the molecule.

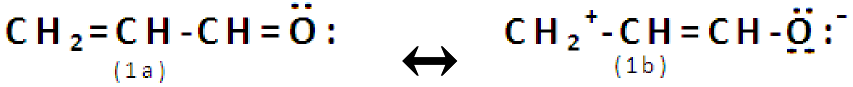
c) Resonating molecules have usually lowered chemical reactivity which is a sequence of their stability.

d) Resonating molecules have bond length which are somewhat shorter than the same bonds found in non-resonating molecules

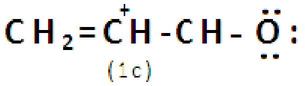
We shall later observe many specific examples of resonating systems:

A – Acrolien.

Acrolien **($CH_2=CH\text{-}CH=O$)** is will approximated by structures (1a) through (1d)



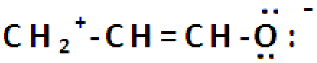
$$\underset{(1a)}{CH_2=CH\text{-}CH=\ddot{O}:} \quad \leftrightarrow \quad \underset{(1b)}{CH_2^{+}\text{-}CH=CH\text{-}\underset{..}{\ddot{O}}:^{-}}$$



(1c)

$CH_2=\overset{+}{C}H-CH-\ddot{\underset{..}{O}}:$

↔



(1d)

$CH_2^{+}-CH=CH-\ddot{\underset{..}{O}}:^{-}$

The hybrid structure may be written as (2a)

$$\mathbf{CH_2^{+}.....CH....CH....O^{-}}$$

In which the highly dotted line indicates that structures (1a),(1b) contribute little to hydride and thus the extent of double bond character of the central bond is expected to be small. The greatest contribution is made by (1a).

B-The Allyl cation

An especially important type of carbonium ion is the allyl ion **($CH_2=CH-CH_2^{+}$)**

Two equivalent resonating structures (3a) and (3b) can be written for this cation:

$CH_2=CH-CH_2^{+}$↔ $CH2^{+}-CH=CH_2$

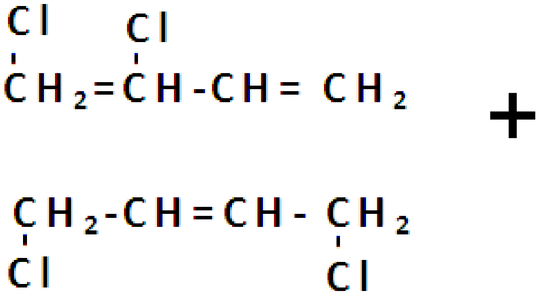
The resonance hydride can be written as:

$$\mathbf{{}^{+1/2}CH_2........CH.......{}^{+1/2}CH_2}$$

As a result of this resonance we expected that the allyl carbonium ion is more stable than the ethyl carboinum whose structure is well represented by a single classical structure **$CH_3CH_2^{+}$**. This was shown to be true since reaction involve carbonium ion intermediates usually proceed much readily when an allylic type cation was produced than when an ethyl or n-propyl cation would be formed.

The hydride nature of allyl carbonium ion can be used to explain why 1,3butadiene reacts with chlorine to give a mixture of the normal 1,2 –dicholro-3-butene and the abnormal product 1,4dicholro-2-butane.

$$\mathbf{CH_2{=}CH\text{-}CH{=}\ CH_2 + Cl_2 \ \rightarrow}$$



$$\overset{Cl}{CH_2}{=}\overset{Cl}{C}H\text{-}CH{=}\ CH_2 \quad + \quad \underset{Cl}{CH_2}\text{-}CH{=}CH\text{-}\ \underset{Cl}{CH_2}$$

According to this suggested mechanism the chlorine molecule may be considered to attack one of the double bonds of butadiene to form first a carbonium ion intermediate is stabilized, substituted allyl carbonium ion which can be represented as hybrid of both structures (4a) and (4b).

$$CH_2=CH-CH=CH_2 + Cl_2 \rightarrow Cl\,CH_2-{}^{+}CH-CH=CH_2 + ClCH_2CH=CH-CH_2^{+}$$

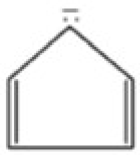
So the negative chloride ion has the choice of attacking C_2 to give 1, 2 –dicholro-3-butene or C_4 to give 1, 4dicholro-2-butane.

$$ClCH_2-{}^{+}CH-CH=CH_2 + Cl^{-} \rightarrow ClCH_2-CHCl-CH=CH_2$$

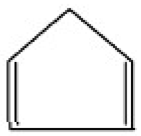
$$ClCH_2CH=CH-CH_2^{+} + Cl^{-} \rightarrow ClCH_2CH=CH-CH_2Cl$$

C-the cyclopentadiene anion

The hydrogens of CH_2 group of 1.3-cyclopentadiene are 10^{30} times more acidic than the hydrogens in ordinary alkanes. The reaction is the loss of one hydrogen of the CH_2- protons results in an anion which is stabilized by resonance hydride of an energetically equivalent structure



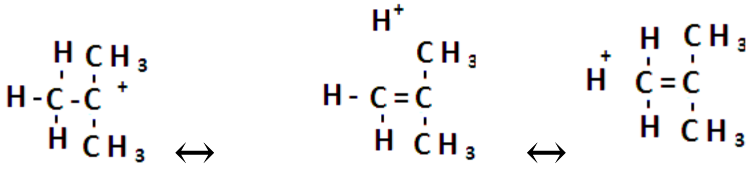
Cyclopentadienyl anion



4-Hyperconjugative effect or Hyper conjugation

We shall examine at this point an extension of resonance theory which plays an important role in the interpretation and understanding of variety of experimental observation that cannot otherwise be explained. This involves the concept of hypercnjugation which is specifically an apparent conjugation of **C-H** bond so, the sigma orbitals of the **C-H** bond overlaps weakly with the vacant **p-orbital** of carbonium ion.

In this case of tertiary butyl carbonium ion resonance structures of this interaction are shown below



We can write nine such structures for ter.butyl carbonium ion. In the above structure we can see the appearance of “no-bond character” between the 4-carbon and its attached hydrogens.

This is why hyperconjugation has been called“ no-bond resonance”.

Hyperconjugation has been used for the interpretation of a number of phenomena some of this is :

a) Stability and ease of formation of carbonium ions and free radicals.

Hyperconjugation has been postulated to play an important role in the stabilization of alkyl cations.we have seen that there are nine hypercojugative structures for ter.butyl carbonium ion.

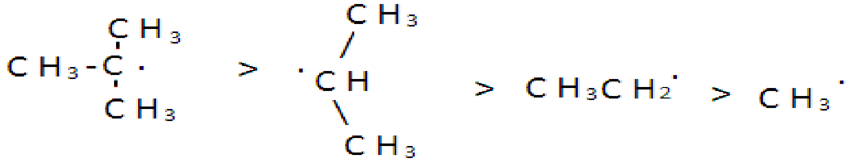
There are six such structures of iso- propyl carbonium ion, three for ethyl carbonium ion and none for methyl carbonium ion.

$^{+}CH_3CHCH_3$ (6). &$^{+}CH_3CH_2$ (3)&$^{+}CH_3$ (0)

The larger the number of contributing structures means more extensive delocalization of positive charge, and hence greater stabilization of the carbonium ion.so we can say that carbonium ion is stabilized by hyperconjugation and we can notice the following order of stability:

Tert.butyl ˃isopropyl˃ethyl˃methyl

Hyperconjugation also operates in the case of free radicals and we can see the following order of stability:



b) Stability of alkenes

Hyperconjugation was also used for explain the relative stability of isomeric olefins and isomeric acetylenes. The degree of stability of these compounds can be determined if we measure the heats of combustion of isobutylene is 646.1 kcal /mol which is significantly less than that for 1-butene ,649.8kcal/mol even though the two isomers have the same number of **C-C,C=C** and **C-H** bonds.

The only difference is that iso-butylene has six hyperconjugative hydrogens whereas 1-butene has $\mathbf{(CH_3)_2C=CH_2}$**&** $\mathbf{CH_3CH_2CH=CH_2}$ only two.

The heats of hydrogenation of a number of alkenes are given in the following table.

Compound	Hyperconjugated hydrogen atom	Kcal/mol

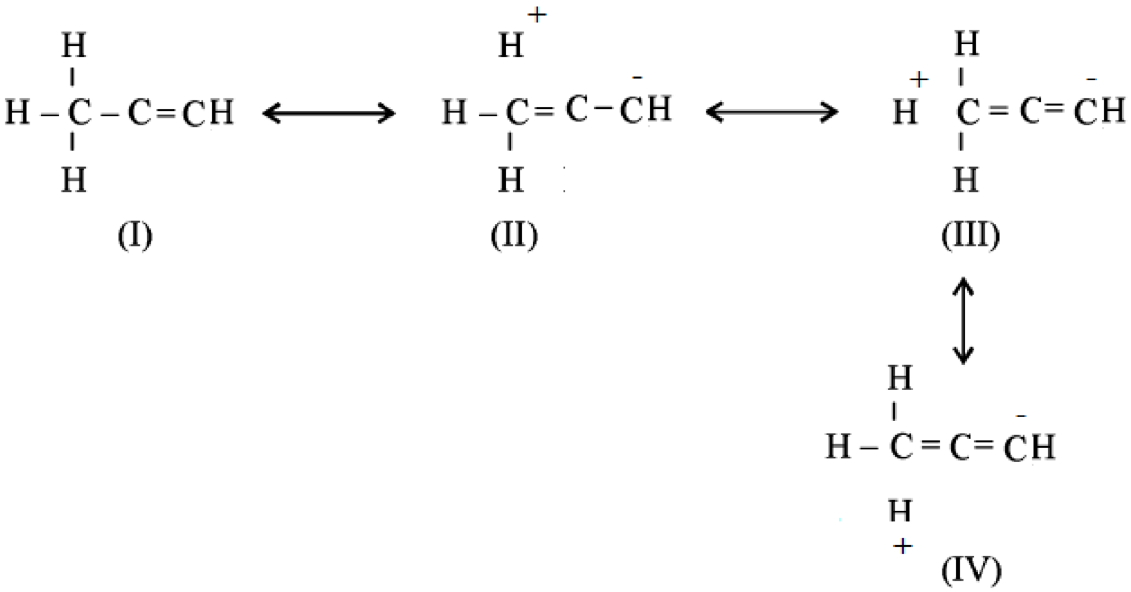
$CH_2=CH_2$	0	-32.6
$CH_3-CH=CH_2$	3	-30.1
$CH_3CH_2CH=CH_2$	2	-30.3
$CH_3CH=CHCH_3$ cis	6	-28.6
$CH_3CH=CHCH_3$ trans	6	-27.6
$(CH_3)_2C=CHCH_3$	9	-26.9
$(CH_3)_2C=C(CH_3)_2$	12	-26.6

We notice from the above table that as the number of hyperconjugated hydrogens increases the heat of hydrogenation decreases which means a higher stability of the compound.

c) Unexpected bond length :

A carbon-carbon single bond ,if adjacent to a carbon –carbon triple bondis usually shorter than the normal length of **1.54A°.**

The **C-C** bond length in methyl acetylene and acetonitrile are **1.46 A°** and **1.48 A°** respectively they are shorter than the single bonds in praffins.these shrinkages are sometimes explained in terms of hyperconjugation since the following contributing can be obtained. And the single **C-C** bond has gained some double bond character.



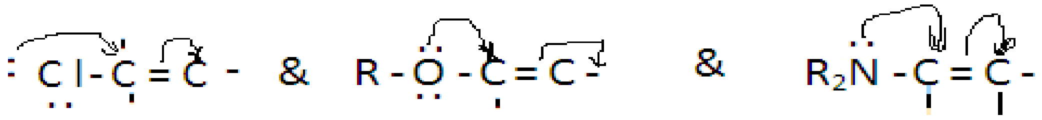
5-Electromeric effect

The mechanism of electron displacement which we have referred to above as resonance effect or mesomeric effect is a permanent effect in the nonreacting or resting molecules.

However, under reaction conditions. Another mechanism of electron transfer might also operate .this is a time –variable polarizability effect, which is called electromeric effect.

Like permanent resonance or mesomeric effect, the time –variable electromeric effect may operate only in system containing multiple bonds.

The effect may be transmitted down an-unsaturated chain of atoms only if the unsaturation is conjugated.propely placed unsaturated atoms carrying unshared electrons (**CL, N, O or S atoms**) may also take part in resonance and electrmeric effects.

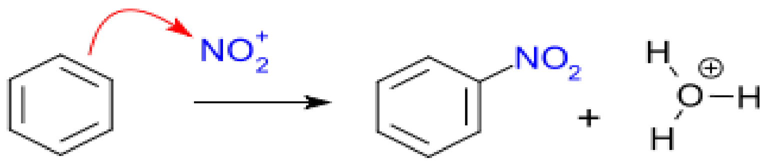


In order to illustrate the electrometric effect, we are going to consider the case of reacting and non-reacting benzene molecule which is resonance hybrid of two resonating structures:

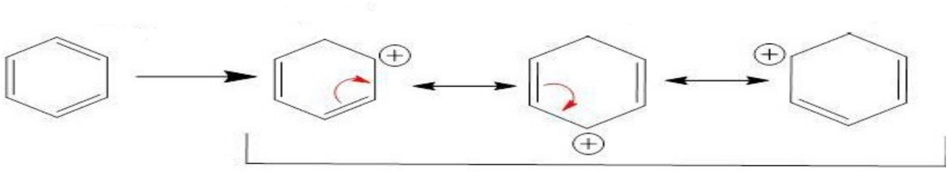
Consider now the benzene molecule under reaction with nitronium ion (**NO_2^+**)

To give nitrobenzene. As the attacking nitronium ion approaches the benzene

Molecule, the electromeric effect will be called into play in such a way as to create a center of negativity at a particular carbon atom being attached.



So at the time of reaction we can consider other resonating structures for benzene like the following structures:

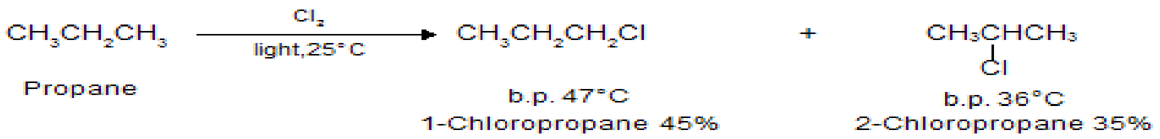


resonance stabilized carbocation

Such structures are called electromeric resonating structures and they work mainly in the time of reaction. The contribution of such structures to a non-reacting benzene molecule is very negligible.in brief, we can say that electomeric displacement is un-saturated systems which place either positive or negative charge on carbon are largely electromeric rather than mesomeric in nature.

Organic reaction mechanism

During our study of organic chemistry we have seen various types of chemical reactions. For example we have seen that alkanes are generally inert, although high temperature reactions of these compounds may result in substitution of hydrogen to give a mixture of halo-alkanes, in removal of hydrogen to give olefins or in breaking of carbon chain:

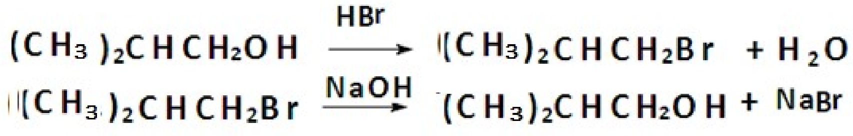


$$CH_3CH_2\ CH_3 \xrightarrow[cata]{High\ temp} CH_3CH{=}CH_2$$

$$CH_3CH_2\ CH_3 \xrightarrow[cata]{High\ temp} CH_2{=}CH_2 + CH_4$$

It is important to notice that replacement of hydrogen by chlorine in reaction with propane is random, thus chlorine can replace any of the hydrogens attached to all three carbons in the propane molecule.

The alkenes and alkynes on other hand are highly ,they undergo what we called addition reactions like hydrogenation, halogenation ,hydrohalogenation ,hydration, …….in contrast to the substitution reactions of alkenes and alkynes take place mainly at low temperatures and involve only the C- bonds in alcohols and halo alkane where a carbon –oxygen or carbon –halogen bond is present. Substitution take place relatively easily and specifically.



$$(CH_3)_2CHCH_2OH \xrightarrow{HBr} (CH_3)_2CHCH_2Br + H_2O$$

$$(CH_3)_2CHCH_2Br \xrightarrow{NaOH} (CH_3)_2CHCH_2OH + NaBr$$

Halo alkanes may react easily by substitution to yield a variety of useful products ,thus treatment with inorganic cyanides furnishes nitriles with ammonia they give amines they give secondary and tertiary amine ,with sodium bisulphides**(NaHS)** they give mercaptans,with sodium sulphides **(Na_2S)** they give thioether,with sodium alkoxide they give ether and so on……….

The concept of reaction mechanism:

In order to brief introduction we have seen two types of substitution reactions.

In the one hand we have the rather random once on alkanes which we must carry out at high temperatures or under the influence of light on the other hand we have those on alcohols and halo alkanes require much energy to get them started while the other type appear require much less energy. This means that we we must be dealing with two different types of substitution reactions.to explain this facts, we should find out for each particular reaction just how the reacting molecules are changed into products. Description of the path by which reactants are transformed into products is called.

the reaction mechanism.

The mechanism of chloration of alkanes is obviously different from the mechanism of substitution in alcohols or halo alkanes.

It is important to point out that the mechanism of organic reaction is simply a theory that can account for the observations we have record. The facts we need for a theory are gathered by studying the effect of different variables on the course of reaction.

These variables include changes in temperature, solvent and slightly changes in reacting molecules.

In this brief introduction to organic reaction mechanism it is obviously not possible to discuss in detail evidences for different theories of many different reaction mechanism. However,before we proceed futher let us define a few terms which are indispensable through our proposed study

Hemolytic and heterolytic cleavage of covalent bonds:

The bond breakage that occur in the course of organic reaction may take place in two different ways:

1. Homolytic or radical reaction:
   $\mathbf{X{:}\,Y \rightarrow \dot{X} + \dot{Y}}$
   Are those in which the bond is symmetrically broken and each of the partners retaining one of the electrons which formerly made up the bond.

2. Heterolytic cleavage (ionic reaction)

$\mathbf{X{:}\,Y \rightarrow X^{+} + Y^{-}}$

Are those in which the bond is broken unsymmetrically, with one of the partners retaining both of the two electrons

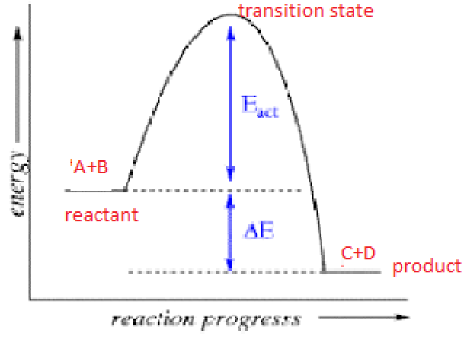
Transition state and activation complex:

In order to understand what is meant by these terms we are going to consider the one step reaction which are molecule of A colloids with one molecule B to form one molecule of C and D

The collision assumed to consist of the approach of an A molecule to a B molecule to form some kind of transient complex particle. This complex particle is called the **activated complex or the transition state**

Which can split apart to give again A and B or it can split in some other way to give anew particle C and D

The situation may be made clearer by reference to potential energy curve given below where potential energy change of the system as A, B molecules come together to form the



transition state and then separate to give C and D molecules.

On the vertical axis of the above diagram is plotted the potential energy of the system ,on the horizontal axis is plotted a coordinate which tells how far the reaction has gone from the initial towards the final state.in the initial state A, and B molecules are far enough not to affect each other.

The potential energy is the sum of A by itself plus B by itself.

As A and B come together the forces of repulsion between the electron clouds become appreciable and work must be done.

This means that the potential energy must increase. It increase until it reaches a maximum that corresponding to the transition state.

The transition state then splits into C and D and the potential energy drops as C and D go apart.

Differences (show by arrow) between the potential energy of the reactant A and B and the potential energy of the transition state is the activation energy which is the energy required to bring the reacting molecules to so called transition state in order to get them to react.

The activation energy is usually supplied by converting some of the kinetic energy of the particles into potential energy.

If A and B molecules do not have high enough kinetic energy they cannot reach to the top of the hill and hence they cannot react.

Similarly. If A and B molecules have enough kinetic energy they can attain the top of the hill forming the transition state which can split to the products C and D.

One more aspect of the above potential energy diagram is of interst.for the case represented, the final state C and D has lower potential energy than the initial state A and B.

There is a net decrease in potential energy as the reaction proceeds this energy usually show up as a heat and this case the reaction is exothermic in other case however, the reaction is endothermic

Rate determining step and order of reaction

The majority of chemical reactions that can be written as balanced equations represented reactants and products molecules and which can be observed in laboratory ,actually do not take place in one step.in some cases a series of steps which reactive intermediate molecules, ions or radical take place. Each of these individual steps occurs with its characteristic rate, and these may these rate may vary widely.in many cases one of the steps occurs with a rate that is significantly slower than any of other steps and so, the rate of the overall reaction becomes the measure of the rate of this one slow step. This step is called the rate determining step for the reaction.

The order of the overall of a given reaction represented by the number of chemical species taking part during the rate determining step and hence the rate of the reaction depends up on their concentration.

Thus a first order reaction is a reaction whose rate depends on the concentration of just one reactant.

A second order reaction is a reaction whose rate depends on the concentration of two reactants and so on.

Nucleophiles and electrophiles

Nucleophiles or nucleophilic reagents are substances which form bonds with carbon by donating an electron pair to site which is electron deficient.

They may be negatively charged like **I^-, Br^-, OH^-, CN^-, CH_3 CH_2 O^-** or **CH_3 COO^-** or they may be neutral but with unshared electron pair like water , alcohols or ammonia

H-O-H & R-O-H & NH_3

A third type (class) of nucleophiles is carbanion which are compounds containing negatively charged carbon.

Electrophiles and electrophilic reagents:

Substance which form bonds with carbon by accepting a pair of electrons are called electrophiles. Examples of these compounds are positively charged ions like proton (**H^+**), nitronium **NO_2^+**, carbonium

They may be neutral like compounds containing elements with incomplete valence shells and empty orbitals like **BF_3. SO_3** and **$AlCl_3$**

Main type of organic reaction:

There are a few basic types of organic reactions of these the most important are:

1. Substitution or displacement reactions
2. Addition reactions
3. Elimination reactions

Substitution or displacement reaction

Broadly defined this type of reaction involve the displacement of one functional group X by another Y

$$\mathbf{R\text{-}X+Y \rightarrow R\text{-}Y + X}$$

Y: is known as the attacking group and X as the leaving group

We have seen before that there are apparently two different types of substitution reactions.

The first of these was the more or less random replacement of alkane hydrogen by halogen at high temperatures. Such a reactions involve homolytic bond cleavage and are known as free radical substitution reaction.

The second type was the specific replacement of halogen in halo alkane by **OH^-**,-**NH_2, -CN** and so on or of **–OH** in alcohols by halogen. These replacements take place under relatively mild conditions, generally in solution. Such specific replacement take place by heterolytic bond cleavage and known as ionic or polar substitution reactions.

ionic or polar substitution reactions:

Such reactions involves heterolytic cleavage and can be classified into two main types according to the nature of attacking agent **Y** in the general equation: **$R\text{-}X+Y \rightarrow R\text{-}Y +X$**

If **Y** is nucleophile reaction is known as nucleophilic substitution.

If **Y** is electrophile reaction is known as electrophilic substitution.

Nucleophilic substitution reaction:

A typical example of this type is the reaction of hydroxide ion with ethylbromide to displace bromide ion giving ethyl alcohol:

$\mathbf{OH^{-} + CH_3\,CH_2\,Br \rightarrow CH_3\,CH_2\,OH + Br^{-}}$

The electron pair of **C-O** bond to be formed can be regarded as donated by the hydroxide ion.wherase the electron pair of **C-Br** bond to be broken departs with leaving bromide ion.The name of these type of reaction is abbreviated as S_N ,

S for substitution and **N** for nucleophilic.

Some other examples of nucleophilic substitution reactions using alkyl halides, alcohols, ethers, esters and onium salts are given in the following table.

Note that nucleophilic reagent **Y** could be an anion **Y^-** or a neutral molecule Y or **HY**.

S_N Displacement reactions

R-X+Y →R-Y +X

Type of compound R-X	Nucleophilic reagent	Reaction
Alkyl bromide	**I^-**	**$R\text{-}Br + I^- \rightarrow R\text{-} I + Br^-$**
Alkyl iodide	**CH_3O^-**	**$RI + CH_3O^- \rightarrow RO\ CH_3 + I^-$**
Alkyl iodide	**CN^-**	**$RI + CN^- \rightarrow RCN + I^-$**
Alkyl bromide	**NH_2^-**	**$R\text{-}Br + NH_2^- \rightarrow R\ NH_2 + Br^-$**
Dialkyl sulphide	**CH_3O^-**	**$RSO_4\ R + CH_3O^- \rightarrow RO\ CH_3 + RSO_4$**

Alcohol	**HBr**	**$ROH + HBr \rightarrow R\text{-}Br + H\text{-}O\text{-}H$**
Ether	**HBr**	**$ROR + HBr \rightarrow R\text{-}Br + R\text{-}OH$**
Ammonium ion	**OH**	**$RNR_3` + OH^- \rightarrow ROH + R_3N$**
Diazonium ion	**H_2O**	**$R\text{-}N{=}N^+ + H_2O \rightarrow ROH + H^+ + N_2$**

The mechanism of **SN** reaction and reactivity of given alkyl compound **R-X** towards a nucleophile **Y** depends upon the nature of **R,X** and **Y** and also upon the nature of solvent.

For **SN** reaction to occur at a reasonable rate it is very important to select a solvent that will dissolve both the alkyl compound and the nucleophilic reagent. In practice, relatively polar solvent or solvent mixtures such as acetone, aqueous acetone, ethanol, aqueous dioxane are good solvents for reactions between alkyl derivatives and salt- like nucleophiles such as **NaCN,NaBr**,……………

Possible mechanism of nucleophilic substitution reaction:

Two mechanism may be written for the reaction of ethyl bromide with hydroxide ion that differ in the timing of bond breaking in relation to bond formation.

In the first mechanism A, the reaction is taking place in two steps, the first of which involves a slow and reversible dissociation of ethyl bromide into ethyl carbonium ion and bromide ion. The second step involves a fast reaction between ethyl carbonium ion and hydroxide ion to yield ethyl alcohol.

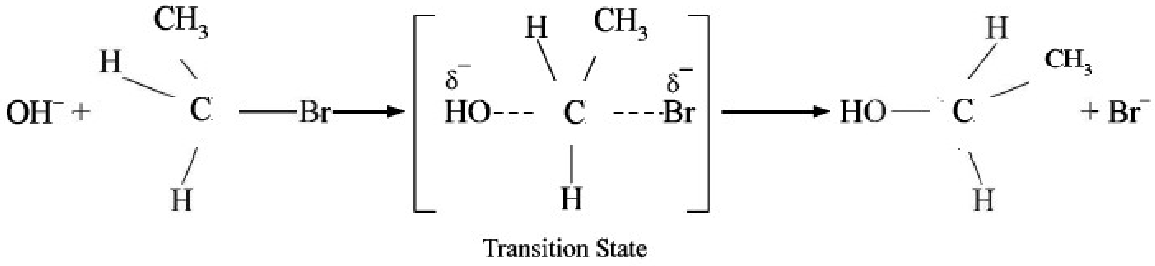
Mechanism A: (two step mechanism)

$\mathbf{CH_3CH_2} \rightleftharpoons \mathbf{Br} \quad \mathbf{CH_3CH_2^+ + Br^-}$ slow

$\mathbf{CH_3CH_2^+ + OH^- \rightarrow CH3CH_2OH}$ fast

In the second mechanism B , the reaction proceed in one step in which ion attack at carbon atom occurs simultaneously with the loss of bromide ion and the carbon oxygen bond is formed at the same time that carbon bromide bond is broken.

Mechanism B:



Some methods for determining reaction mechanism:

A number of methods can be used to distinguish between the one-step and two-step mechanisms given in the previous section.

The uses of one method or others depends upon the nature of reactants and products as well as upon reaction conditions some of these methods are given below.

1. **Kinetic methods**

Determination of the order of the reaction the **S_N1** and **S_N2** mechanism.

This method is general and can be used to determine the mechanism of the reaction of ethyl bromide with hydroxide ion.of the two mechanism given previously for this reaction.a requires the rate to depend on the concentration only of one of reactants. The rate at which ethyl alcohol formed will depend on the concentration of ethyl bromide and not on the hydroxide ion concentration. Because hydroxide ion is not utilized except in a fast secondary step.

The reaction rate is thus a first order .in contrast mechanism B requires the rate to depend on the concentration of both reagents. Since the slow step involves collision between hydroxide ion and ethyl bromide, so, the correctness of mechanism B which is a one-step mechanism would be established by showing that the rate of the reaction is dependent on the concentrations of both ethyl bromide and hydroxide ion.

We have then a kinetic method for distinguish between the two possible mechanism A and B experimentally, the rate of formation of ethyl alcohol is found to be proportional to the concentration of both ethyl bromide and hydroxide ions.

The reaction rate is thus second order reaction

$$\mathbf{r= [CH_3CH_2Br][OH^-]}$$

From this we conclude that the mechanism of the reaction is one step process B.

This type of reaction is generally classified as second-order nucleophilic substitution reaction and often designates as $\mathbf{S_N{}^2}$

S: for substitution, **N**: nucleophilic and 2: for second order.

The alternate- two-step process of mechanism A is the first order reaction designated as $\mathbf{S_N{}^1}$

Examples of $\mathbf{S_N{}^1}$ reaction: a good example of $\mathbf{S_N{}^1}$ reaction is the reaction of ter-butylchloride with hydroxide ion to yield ter-butyl alcohol.

The rate of this reaction is proportional only to the concentration of ter-butylchloride, this is an evidence that ter-butyl chloride hydrolysis by $S_N{}^1$ mechanism.

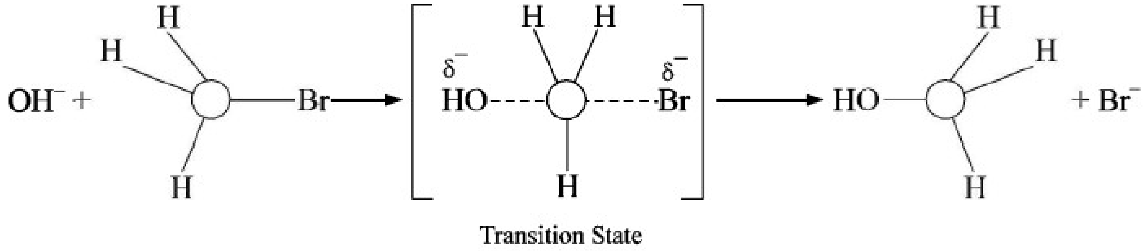
$$\mathbf{(CH_3)_3C \rightleftharpoons -Cl \quad (CH_3)_3C^+ + Cl^-}$$

$$\mathbf{(CH_3)_3C \rightleftharpoons {}^+ + OH^- \quad (CH_3)_3C{-}OH}$$

2. Stereo chemical methods and the walden inversion:

In order to understand the use of stereochemistry in determining reaction mechanism we should be first know the stereochemical difference between both$\mathbf{S_N{}^1}$ and

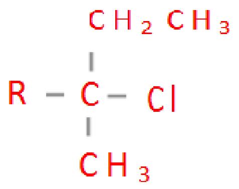
$\mathbf{S_N}^2$ reactions.in the $\mathbf{S_N}^1$ mechanism a free carbonium ion is formed which is most stable in the planar configuration can then be attacked equally from both sides ,in the $\mathbf{S_N}^2$ mechanism the nucleophile attacks the carbon atom carrying the leaving group from the backside and the configuration of this carbon in the product will be the opposite of that in the starting material.so , an $\mathbf{S_N}^2$ reaction of methyl bromide with hydroxide ion will result in the approach of the $\mathbf{OH^-}$ leads to attachment of the ion to the carbon atom from this direction which will cause the three hydrogen atoms of methyl bromide to take up a new positions on the side of the carbon atom away from the $\mathbf{OH^-}$ group. This can be represented three dimensionally as follow:



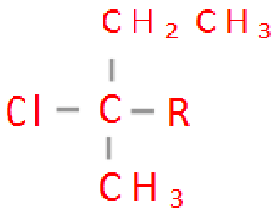
The molecule of methyl bromide is said to inversion in its conversion methyl alcohol. Inversion of configuration is characteristic of $\mathbf{S_N}^2$ reactions.

Although we cannot see any evidence of such inversion in a molecular like methyl bromide, it is possible to obtain direct evidence in laboratory for such inversion molecules.

An example is s-butyl chloride, which has an asymmetric carbon attached to four different groups, chlorine, methyl, ethyl and hydrogen, and therefore it is optically active and can be obtained in right and left handed form.



$$\begin{array}{c} \quad CH_2CH_3 \\ | \\ R - C - Cl \\ | \\ CH_3 \end{array}$$



$$\begin{array}{c} \quad CH_2CH_3 \\ | \\ Cl - C - R \\ | \\ CH_3 \end{array}$$

We can determine the type of mechanism (**S_N^1 or S_N^2**) by which s-butyl chloride react with hydroxide ion to give s-butyl alcohol, if we start with an optically active form. Since according to the above discussion, if this molecule react with **S_N^1** mechanism the resulting carbonium ion is planar and can be attack equally from either side leading to a racemic mixture product. On the other hand, if s-butyl chloride reacts by **S_N^2** mechanism inversion of configuration will take place around the asymmetric carbon atom at which **S_N^2** displacement will take place.

The result of experiments using one of the two optical isomers show that hydroxide ion attacks s-butyl chloride by backside approach to give s-butyl alcohol of inverted configuration.

Similar studies of various examples have established that $\mathbf{S_N{}^2}$ reactions always proceed with the inversion of configuration.

This stereochemical behavior is commonly known as Walden inversion, finally we may in fact make the generalization that any reaction yielding an optically active product cannot proceed through an intermediate carbonium, cannot proceed by $\mathbf{S_N{}^1}$ mechanism.

3. Identification of products:

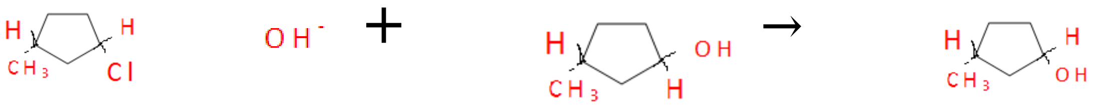
As a matter of fact an analysis of the products of reaction may lead us to know the type of mechanism through which the products were formed.

Consider for example the reaction of cis -3methylcyclopentylchloride with hydroxide ion to give the alcohol.

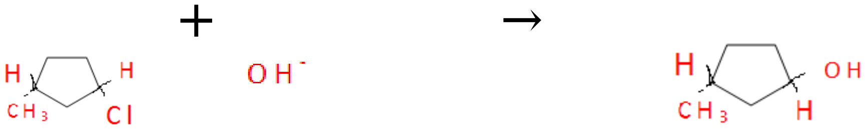
If this reaction occurs by $\mathbf{S_N{}^1}$ mechanism free carbonium ion will be formed which can equally attacked from up to down with respect to the plane of ring yielding a mixture of cis and transmethylcyclopentyl alcohol, on other hand , if the reaction proceed by **S_N^2** mechanism, which involves a backside the attack at the carbon where the chlorine is attached resulting in the formation of only trans alcohol.

Analysis of the product obtained from the reaction was shown to be trans-3-methyl-cyclopentyl alcohol from which we can conclude that the reaction occurs only backside **S_N^2** displacement.

If the reaction occurs by **S_N^1** mechanism:



If the reaction occurs by S_N^2mechanism:



Structural, solvent and electric effects in substitution reaction (SN):

We have already mentioned that in a substitution reaction:

R-X+Y →R-Y +X

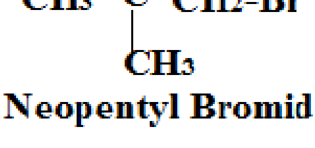
The rate and type of reaction depend upon the nature of **R,X** and **Y** as well as solvent used.

A. Structure of the alkyl group:

The rate of $\mathbf{S_N^2}$ substitution reaction of simple alkyl derivatives, **RX** follow the other: primary R ˃ secondary R ˃ tertiary R.

This explained in terms of hindrance to approach of the attacking group to the backside of carbon atom undergoing displacement, owing to the size of the groups attached to this carbon atom.

In practical synthesis involving $\mathbf{S_N^2}$ reaction the primary compounds generally work well, secondary isomers are fair and tertiary isomers are difficult.Neopentylbromide is very un reactive in $\mathbf{S_N^2}$ reaction because of steric-hindrance by the methyl groups on the **β-carbon**.



$$CH_3\ \overset{CH_3}{\underset{CH_3}{C}}-CH_2-Br$$

Neopentyl Bromide

So in $\mathbf{S_N^2}$ reaction of alkyl halides with $\mathbf{OH^-}$, reactivity of methyl , ethyl ,isopropyl and tertiary bromide is as follow:

$\mathbf{CH_3\,Br > CH_3\,CH_2\,Br > (CH_3)_2CHBr > (CH_3)_3\,C\,Br}$

In complete contrast to $\mathbf{S_N^2}$ reaction reactions, the rates of $\mathbf{S_N^1}$ reaction of alkyl derivatives follow the order:

Tertiary R ˃ secondary R ˃ primary R

And so the order of reactivity of methyl, ethyl, isopropyl and tertiary butyl bromides in $\mathbf{S_N^1}$ reaction will be as follow:

$\mathbf{(CH_3)_3\,C\,Br > (CH_3)_2CHBr > CH_3\,CH_2\,Br > CH_3\,Br}$

A second important factors that favors the above order of reactivity in

$\mathbf{S_N^1}$ reactions is the stability of the intermediate carbonium ions due to hyper conjugative resonance which increase in the series methyl, ethyl, isopropyl and tertiary butyl.

B. **The leaving group :**

The reactivity of a given alkyl derivative **R-X** in either $\mathbf{(S_N^1}$ **or** $\mathbf{S_N^2)}$ reactions is determined in part by the nature of the leaving group **X**. in general, there is a reasonable relation between the reactivity of **R-X** and acid strength of **H-X** , the **X** group that corresponds to the strongest acids being the best leaving groups , thus , since **H-F** is relatively weak acid and **H-I** is a very strong acid ,the usual order of reactivity of alkyl halides is : **RI˃ RBr ˃ RCl ˃ RF**

C. The attacking group

The nature of the attacking group is also important in determining the rate and type of the mechanism.

For example: the $\mathbf{S_N}^2$ reactivity of a particular reagent toward an alkyl derivatives is determined by its nucleophlicity which is its ability to donate an electron pair to carbon.

The nucleophilicity of a reagent does not always parallel its basicity measured by its ability to donate an electron pair to a proton. So a strong base is a good nucleophile **($\mathbf{OH^-}$)** but a very weak base may also be a good nucleophile. **(I^-)** among the halogens, the nucleophilicity is given in order : $I^- > Br^- > Cl^- > F^-$

Thus I^- is a better nucleophile than Br^- and can displace it in S_N2 reaction

$R\text{-}Br + I^- \rightarrow RI + Br^-$

Why is the reactivity sequence $I^- > Br^- > Cl^- > F^-$ in nucleophilic substitution opposite to that expected from either the sequence of the strength of the bond formed **C-F > C-Cl > C-Br > C-I**

Or the sequence of basicity of the nucleophiles

$F^- > Cl^- > Br^- > I^-$ **???**

This can be explained in terms of solvation energies of the ions is given in the following:

$F^- \rightarrow F$ **E= -117 kcal**

$Cl^- \rightarrow Cl$ **E= -85 kcal**

$Br^- \rightarrow Br$ **E= -78 kcal**

$I^- \rightarrow I$ **E= -68 kcal**

It is clear that the solvation energies of small ions with concentrated charge are always greater than those of large ions with diffuse charge.

When ion participate in a nucleophilic attack on carbon it must be free from some of solvent molecules that stabilize it in a solution or also it cannot get close enough to this carbon to which it will be attached to being forming a bond.

This will be a less favorable process for a small ion than for large ion, and on this basis we expect $\mathbf{F^-}$ to be less reactive in nucleophilic attack than I^-

D. The nature of the solvent:

The solvent is an important factor that enters into the determination of mechanism **(S_N^1 or S_N^2)** that given substitution reaction follow.

The rate of most $\mathbf{S_N^1}$ reactions are very sensitive to solvent changes.

Polar solvents (solvent with high dielectric constant) favors the $\mathbf{S_N^1}$ mechanism over the $\mathbf{S_N^2}$ mechanism. This is due to two reason:

First: a high dielectric constant increases the ionization power of the molecule.

Second: the ability of the polar solvents to solvate the separated ions and so they add to their stability. With regard to $\mathbf{S_N2}$ reaction however , we can conclude that they are also sensitive to solvent effects,because no large separation develops in the transition state

E. Electronic effects:

Electronic effects are also important in determining reaction mechanism the significance of such effects will be understood if we considered the following specific cases and examine their behavior towards both S_N1 and $\mathbf{S_N2}$ reactions.

1. Allyl halides:

Allyl and substituted allyl halides are highly reactive in substitution reactions of halogen atom. The large degree of resonance stabilization of allyl carbonium ion provides a low energy pathway for cleavage of the carbon –halogen bond for example, allyl bromide reacts with $\mathbf{OH^-}$ very easily to give allyl alcohol.

CH_2 =CH-CH_2- Br + OH^-→ CH_2 =CH-CH_2-OH + Br^-

In solvents like (water, aqueous alcohol, and aqueous acetone) the reaction follows the S_N^1 mechanism due to the stability of the intermediated carbonium ion for which two main equivalent contributing structure may be written:

CH_2 =CH-$CH_2{}^+$ ↔ CH_2- CH=$CH_2{}^+$

In solvents that favors the S_N^2 mechanism (like dry acetone) the above reaction can also take place since there are no electronic or steric effects that might hinder the S_N^2 path so allyl halides react very readily by S_N^1 and S_N^2 mechanism.

2. Vinyl halides:

In constract to the highly reactive allyl halides are the highly non-reactive vinyl halides **CH_2 =CH-X** conjugation of the un shared pair of electrons of the halogen with the carbon-carbon double bond gives rise to a resonance effect represented as follows: **CH_2 =CH-Cl ↔ $^-CH_2$ -CH=Cl^+ ↔ $^-CH_2$=CH=Cl^+** resonance hydride.

The net result of this conjugation is stronger bonding of the chlorine to the adjacent carbon with subsequent difficulty of displacing the chlorine as **Cl^-** ion.

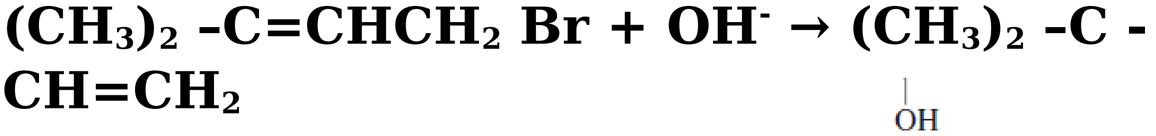
The **C-Cl** bond acquires some double bond character.

With subsequent shorting of the **C-Cl** bond distance.

The **C-Cl** bond length in vinyl chloride is **1.69A°** compared with normal **C-Cl** distance of **1.77 A°** found in most alkyl chlorides.

Allylic rearrangement:

In allyl halides substituted in either of the terminal carbon atoms, the replacement of the halogen atom with another group leads to what is known as allylic rearrangement for example, the hydrolysis of 1-bromo-3-methyl-2-butene did not afford the simple displacement reaction of **-Br** or **–OH** but to rearranged product 3-methyl-3-hydroxy-1-butane:



$$(CH_3)_2 -C=CHCH_2\,Br + OH^- \rightarrow (CH_3)_2 -\underset{\displaystyle OH}{\underset{|}{C}} - CH=CH_2$$

In such reaction follows an $\mathbf{S_N^1}$ path, the above rearrangement can be explained in terms of resonance of intermediate carbonium ion for which the following structure can be written:

$$\mathbf{(CH_3)_2\text{–}C{=}CHCH_2^+ \leftrightarrow (CH_3)_2\text{–}C^+\text{-}CH{=}CH_2}$$

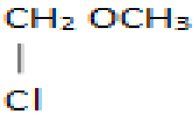
(a) (b)

Structure (b) with tertiary carbonium ion contribute more and the OH^- ion attacks this carbon rather than the primary carbon in structure (a) with subsequent rearrangement .in such reaction, however, a mixture of the two products results but in different ratios, in cases where the carbonium centers are structurally equivalent (as in allyl bromide), rearrangement also occurs but is not observable since attachment of the incoming group at either carbons leads to the same product.

3. α – haloethers

α-haloethers are very reactive in nucleophilic substitution reactions where it reacts by $\mathbf{S_N^1}$ mechanism.

This means that ionization to carbonium and halides ions is easily this is due to the stability of the carbonium ion because of the overlap

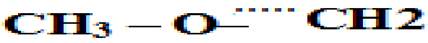


$$\begin{array}{l} CH_2\ OCH_3 \\ | \\ Cl \end{array} \rightarrow (CH_2OCH_3)^+ + Cl^-$$

Of nu shared pair of electron on oxygen atom with the vacant p-orbital of the adjacent positively charged carbon atom to give the following two resonating structures:

$$CH_3 - O - CH_2^- \leftrightarrow CH_3 - O^+ - CH_2$$

As we known from our study of resonance the actual carbonium ion cannot represented by any of the two structures but by a resonance hydride in which the positive charge is distributed over both oxygen and carbon.

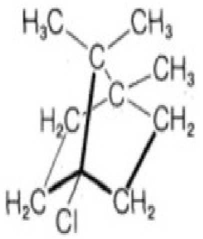


$CH_3 - O \cdots CH2$

Apo camphyl chloride:

Apo camphyl chloride is highly in reactive by both S_N1 and S_N2 mechanism in substitution of chlorine atom,it is unaffected even by boiling with 30%

Apocamphyl chloride, below, is unreactive in either S_N1 or S_N2 reactions.



alcoholic **KOH** for two hours or with boiling alcoholic silver nitrate. This can be interpreted as follows:

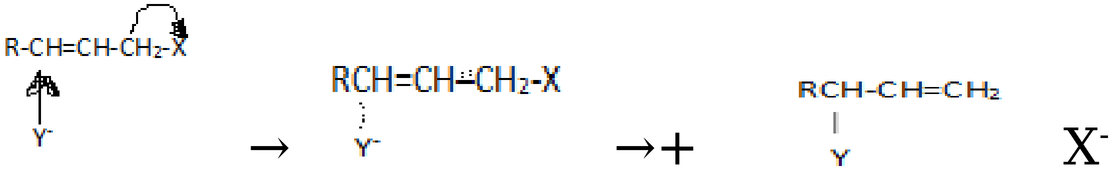
a) Apocamphyl chloride cannot react by $\mathbf{S_N^2}$ mechanism because of the steric hindrance around chlorine atom which makes it hard for a nucleophile to approach to carbon at which the chlorine is attached.

b) Apocamphyl chloride cannot react by $\mathbf{S_N^1}$ mechanism since this requires the formation of carbonium ion at a bridged carbon atom which is not possible. We, already known that only stable carbonium ion can be formed with ease and that resonance stabilization of such ions requires that the ions must be planar .it can be seen from the geometry of apocamphyl chloride that the three bonds to carbonium carbon are prevented from being planar by the cage like structure of the rest of the molecule. Thus the ionization of chlorine to give the ion is impossible.

The S_N^2 reaction:

It is of interest to note that certain cases of nucleophilic substitution of allylic type halides show second order kinetics and lead to rearranged product. Since the observation of rearrangement is not compatible with **S_N^2** mechanism.

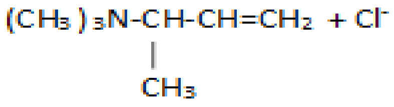
The **S_N^2** mechanism is suggested is **S_N^2** mechanism the nucleophile attacks the unsaturated carbon rather than the saturated carbon with simultaneous shift of the double bond electrons and removal of halide ion:



Transition state

An example of the reaction is :

$(CH_3)_3N$: + $CH_3CH{=}CH\text{-}CH_2CL$→



$$(CH_3)_3N\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH{=}CH_2 + Cl^-$$

Electrophilic substitution reaction ES:

In contrast to nucleophilic substitution reaction **S_N** in which substitution at carbon involves attack of nucleophilic reagent.

Electrophilic substitution reaction involves attack of an electron seeking or electrophilic reagent at carbon.

These reactions are designated, **ES**

S: substitution & **E**: electrophilic

$R{:}X + Y{:} \rightarrow R{:}Y + X{:}$ S_N

$R{:}X + Y \rightarrow R{:}Y + X^+$ S_E

Some typical examples of electrophilic substitution at carbon

$CH_3^+ MgBr^- + Br\text{-}Br \rightarrow CH_3 Br + MgBr_2$

$CH_2{=}CH\text{-}CH_2^-{:}Li^+ + H{:}OH \rightarrow CH_2{=}CH\text{-}CH_3 + LiOH$

We can give two possible mechanisms for electrophilic substitution by analogy with nucleophilic substitution.

The first is a two – step reaction involving ionization to a carbanion intermediate followed by reaction with electrophile to form a product.

This will be designated as an **S_E^1** mechanism.

$R{:}X \rightleftharpoons R{:}^- + X^+$

$R:^{-} + Y^{+} \rightarrow R:Y$

The second mechanism is one step reaction in which the bond to the entering group is formed at the same time as the bond to the leaving group is broken.

This will be an **S_E2** mechanism.

$Y^{+} + R:X \rightarrow Y^{+}\ldots\ldots.R\ldots\ldots X^{+} \rightarrow R:Y + X^{+}$

However, the mechanism of electrophilic substitution have not been investigated as extremely as nucleophilic substitution.

This is partly because they are not so common and involve reaction of organometallic which are not suitable for kinetic and stereo chemical investigation.

Recently, the use of optically active organometallic compounds indicated that.

Electrophilic substitution at carbon normally proceed by front side attack with retention of optical activity.

Addition reactions

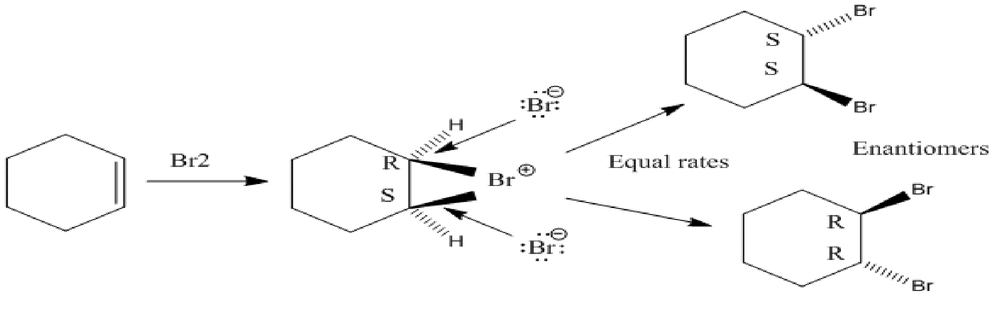
1. Electrophilic addition reactions.

Most addition reactions to olefins and acetylenes involve initial attack by an electrophile and they are therefore called electrophilic addition reactions.

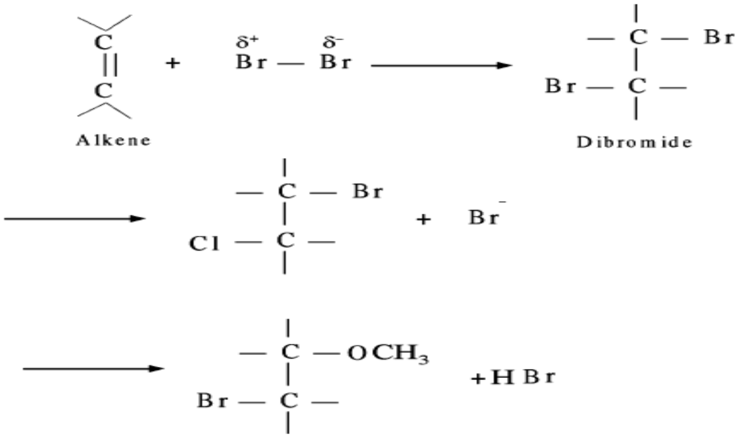
Examples are the addition of halogens **(Cl_2 ,Br_2 and I_2)** ,hydrogen halides **(HCl and HBr)** hypohalous acids**(HOCl and HOBr)**, water and sulfuric acid.

a) Bromine addition proceeds in the dark and in the presence of free radical inhibitors.so the reaction should be an ionic or polar reaction.

b) Bromine addition as well as addition of other reagent gives trans addition. For example , cyclohexene adds bromine to give 1,2 dibromocyclohexane.



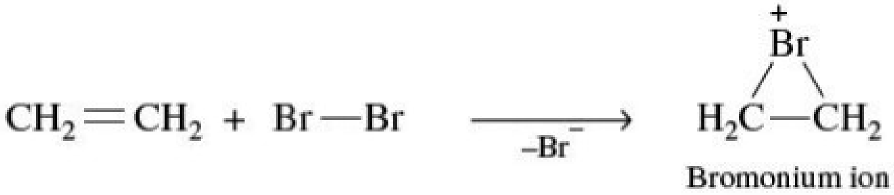
c) Bromine addition to an alkene in methyl alcohol containing lithium chloride leads not only to the



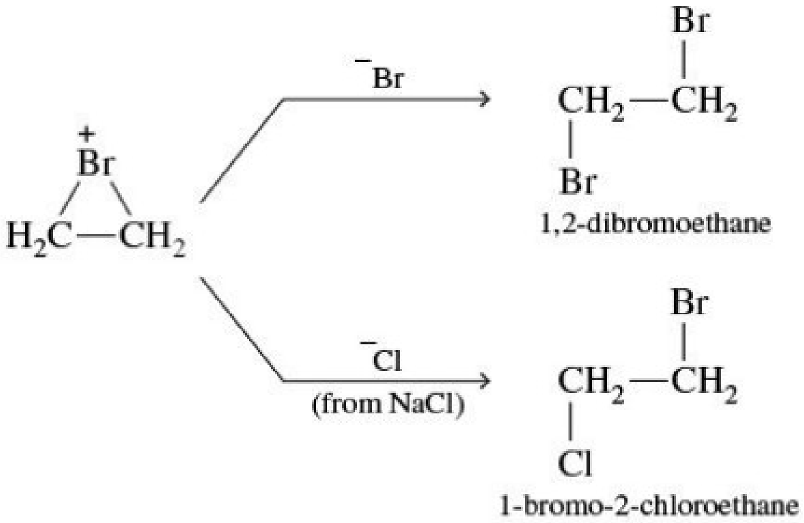
expected dibromo alkane. but also to products resulting from attack by chloride and solvent ions.

A some what simplified mechanism that accounts for most of the above facts is given for the addition of bromine to ethylene.in first step , bromine molecules forms a loose complex with the electrons of the double bond of alkene

Complexes of this type known as charge – transfer complexes or complexes yield an intermediate- complex in which bromine is bonded to both carbons of the double bond. This intermediate is called bromonium ion.



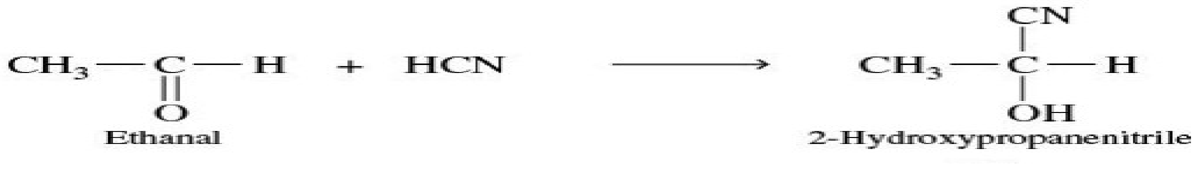
In the second step of attack of bromide ion or other nucleophile, at carbon on opposite side of the bridged group results in formation of trans-addition product.

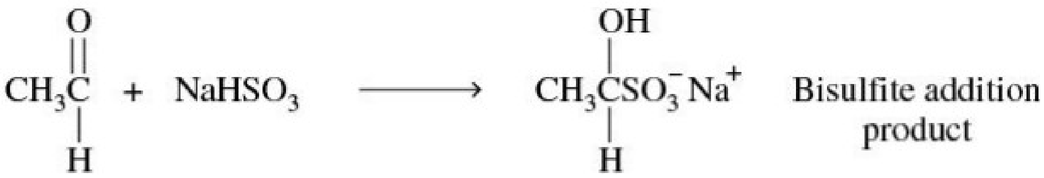


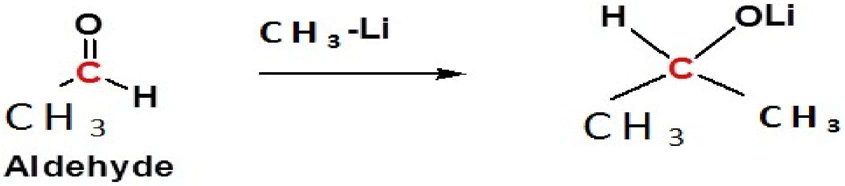
2. **Nucleophilic addition reactions:**

Addition reactions to multiple bonds between carbon and some other elements (oxygen as aldehydes, ketones, esters, and amides ,nitrogen as nitriles or imines) generally involve attack on carbon by nucleophile and are classified as nucleophilic addition reactions.

For examples of such reactions are the addition of hydrogen cyanide, sodium bisulphite and methyl lithium to carbonyl group of aldehyde and ketones







We are going to study the mechanism of addition of **HCN** to carbonyl compounds (acetone) to yield cyanohydrin as an example of nucleophilic addition reaction.

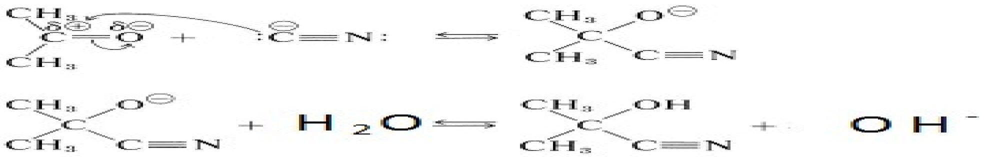
The formation of cyanohydrin requires a basic catalyst.in the absence of a base, the reaction does not proceed or is at best very slow.

This is clear because hydrogen cyanide itself has no unshared pair of electrons on carbon so it is unable to form a carbon – carbon bond to a carbonyl carbon.

The presence of base is necessary to convert hydrogen cyanide into cyanide ion which can function as a nucleophile towards carbon.

A complete reaction of cyano – hydrine formation can be represented as follow:

$HCN + OH^- \rightarrow CN^- + H_2O$

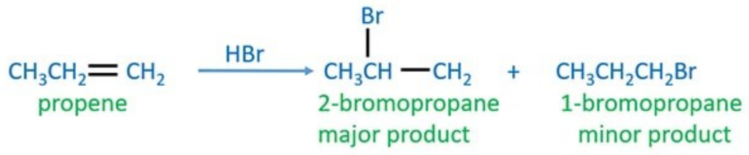


In the above sequence, the last step regenerate the base catalyst again.

Orientation in addition to alkene

Markonikoffs rule

Addition of an asymmetrical substance like **HX** to an unsymmetrical alkene can give rise to two isomers depending upon the direction of addition of the molecule. Thus ,addition of **HBr** to propylene could lead to either 1-bromo propane or 2-bromopropane.



It has been found experimentally that the major product formed in this reaction is 2- bromopropane.

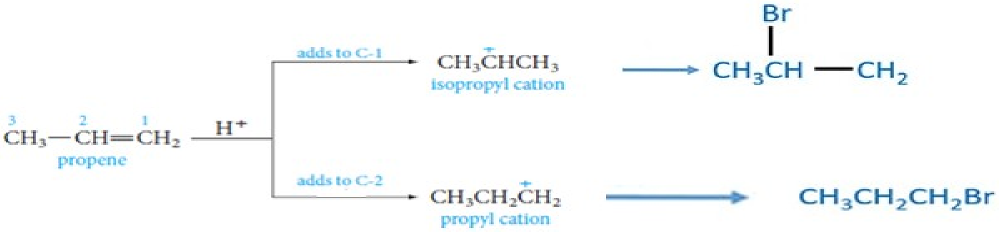
One of the most important early rules in organic chemistry was markoniffs rule which states that in the addition of an unsymmetrical molecule **HX** to an unsymmetrical carbon- carbon double bond that carries the greater number of hydrogen or in more general terms the rule stated that the position portion of adding molecule to an unsymmetrical carbon- carbon double bond will going to the carbon atom having the larger number of hydrogens and negative portion will go to the carbon atom having a fewer number of hydrogen atoms. Since **HBr** tends to ionize into **H^+** and **Br^-** .

The rule is apply to the propylene molecule such as above.

It is an important to note that markoniffs rule is not general and as we see later cannot be applied to all cases. It is of considerable utility only when applied to polar or ionic reagent added to hydrocarbons having only one double bond.

Theoretical basis of markoinkoffs rule :

To understand this rule consider the addition of HBr to propylene. The reaction occurs in a stepwise nature in the first step the hydrogen ion attaches itself to one of the two electrons of the double bond leaving the other carbon atom as carbonium ion center



In a sequence step the bromide ion Br^- adds to the positively charged carbon atom it is clear from the above mechanism that the two different carbonium ion intermediate could be formed by attachment of a proton to one or the other of bouble – bond carbons.

These could be a primary or a secondary carbonium ions.

Since we know that the order of decreasing stability or increasing energy content of isomeric carbonium ions is tertiary, secondary, primary , so we can predict that the secondary propyl carbonium ion

$\mathbf{CH_3CH^+CH_3}$ will be more stable than the primary carbonium ion

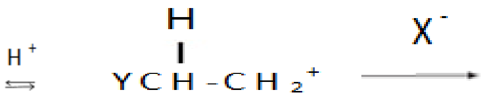
$\mathbf{CH_3\ CH_2\ CH_2{}^+}$ .hence 2-bromopropane will be the product.

Addition to substituted alkenes and violation of the markonikoffs rule :

As we mentioned before this rule is only obeyed when applied to polar addition to hydrocarbons. For alkenes that carry halogens or other similar substituents the rule cannot be applied.

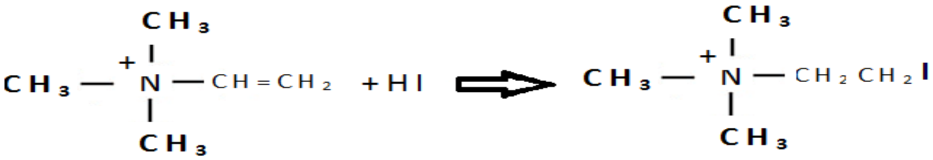
Consider a compound of the type $\mathbf{Y\text{-}CH{=}CH_2}$, IF **Y** is more attracting than hydrogen then hydrogen halide**(HX)** should add in such a way so as to attach the proton on the **Y-CH=** group and **X** on the $\mathbf{\text{-}CH_2}$ group.

This result is actually in violation of markonikoffs rule

$Y\text{-}CH{=}CH_2$  **$Y\text{-}CH\text{-}CH_2\text{-}X$**

So ,when a powerful electron- attracting substituent is employed as **Y** , the addition goes as above , provided the carbon of the double bond carried no un shared electron pair.

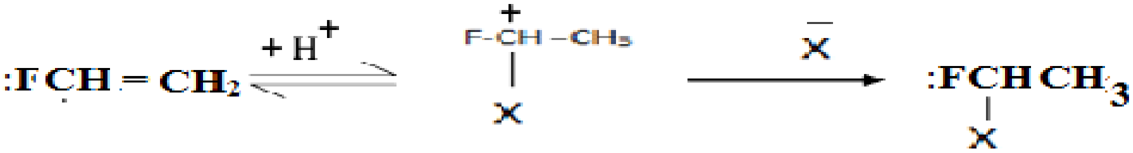
$CF_3\text{-}CH{=}CH_2 + HCl \rightarrow CF_3\,CH_2\,CH_2\,Cl$



Thus on the other hand with **Y** groups having elements such as oxygen or halogen with unshared pair of electrons.

Addition take place in accordance with markonikoffs rule as shown below :

$Y\text{-}CH{=}CH_2$in which **$Y = R{:}O^-$, $:F^-$,$:Cl^-$,** **.....**

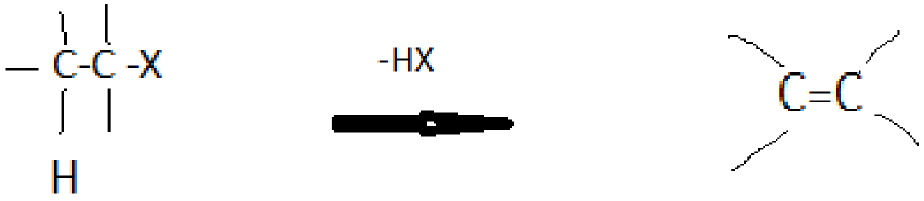


In such cases , the electron attracting power of the substituent induced by negative inductive effect is overcome by the ability of substituent to donate their unshared pair of electrons to the adjacent positive carbon.

Elimination reactions

Elimination reaction is the reverse of addition this generally involve the loss of two substituents from two adjacent carbon atoms in a chain or ring.

Usually a proton is lost from one of the atoms and nucleophile **(X :)** is lost from the other and this is why we call this elimination $\mathbf{E_2}$ or β-elimination reaction.



X = Br^-, Cl^- , I^-, CH_3COO^- , $^+SR_2$,$-NR_3$, $-O^+H_2$

The nucleophile is commonly a halide, hydroxyl, ester or onium group.

Substitution and elimination reactions usually proceed concurrently for alkyl derivatives and in synthetic work substitution reactions are often accompanied by olefin formation which indicate that both substitution and elimination reactions must have rather closely related mechanisms. Before futher discussion of factors influence the competition between elimination and substitution reaction let us examine the mechanism of elimination reaction.

The E_2 elimination reactions:

Consider the reaction of ethyl chloride with sodium hydroxide

$CH_3 CH_2 Cl + OH^- \rightarrow CH_3 CH_2OH + Cl^-$
(S_N^2)

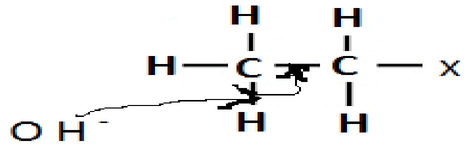
$OR \rightarrow CH_2 = CH_2 + HO + Cl$

Elimination to give ethylene competes with substitution to give ethyl alcohol furthermore , the rate of elimination like the rate of substitution is proportional to the concentration of ethylchloride and hydroxide ion thus elimination is here a second order reaction.

The term $\mathbf{E_2}$ has been proposed for such second- order elimination reaction.

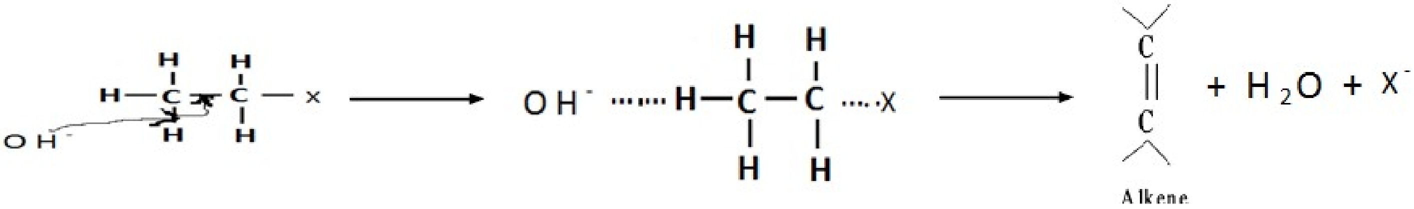
Available evidence indicates the rate determining step to be an attack by the $\mathbf{OH^-}$ ion on ahydrogen atom attached to the carbon atom , which is adjacent to the one holding the halogen atom**(the β- carbon atom).**

This hydrogen is removed as a proton and simultaneously of electrons holding it forms the – electron pair of the double bond and the halogen with its bonding electrons is lost as a halide I^- these electrons shifts are represented by curved arrows as follows:



A more complete representation of the transformation is shown below in which the bonds being formed in the transition state are dotted lines.

This is agreement with the kinetic results which requires atransition state involve one molecule of alkyl halide and one hydroxide ion.



The E_1 elimination reactions

Many secondary and tertiary halides undergo elimination reactions by a mechanism show to be different from that of the **E_2** eliminations.

These reactions , as do the **S_N^1** reactions , have as their rate – determining step.

The slow ionization of alkyl halide and show first order kinetics with rate dependent only on alkyl halide concentration. Such elimination reactions have therefore, been termed **E_1** reactions .in these reactions the carbonium ion formed in the initial slow step may then with the aid of solvent lose a proton to yield the olefin, for example, if we start with tertiary butyl chloride , the **E_1** reaction proceed as follow:

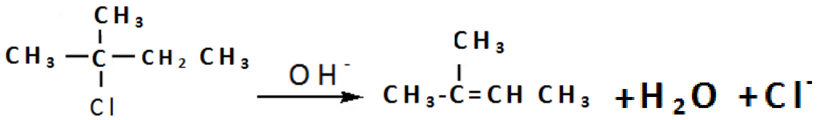
$$(CH_3)_3C\text{-}Cl \rightleftharpoons (CH_3)_3C^+ + Cl^- \text{slow step}$$

$$(CH_3)_3C^+ + H_2O \rightleftharpoons (CH_3)_2C{=}CH_2 + H_3O^+$$

The **E_1** reaction competes very successfully with the **S_N^1**types in fact it is always very difficult to carry out substitution reactions. On many tertiary alkyl halides in good yields because of large amount of olefin formed

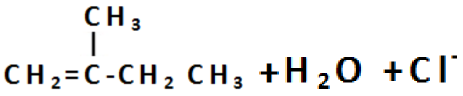
Orientation in elimination reactions and the sayetzeff rule

With halides have asymmetric **R** group, like tertiary amyl chloride it is possible to have two or more different olefins formed, depending upon which β- hydrogen is removed. Most **E_1** and **E_2** elimination reactions , tends to yield the most highly substituted alkenes.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2\,CH_3 \xrightarrow{OH^-} CH_3-\overset{\overset{CH_3}{|}}{C}=CH\,CH_3 + H_2O + Cl^-$$

Or



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2\,CH_3 + H_2O + Cl^-$$

A similar effect was also noted in the dehydration of alcohols .many experimental observation of this type were formulated in 1875 into a useful generalization by Russian chemist sayetzeff.

The sayetzeff rule state that in reaction of removal of hydrogen halide from asymmetrical alkyl halides (and water from alcohols).

The hydrogen will come from the more highly branched carbon atom.

Resulting in preferential removal of tertiary over secondary and secondaryover primary hydrogen atoms.

The reason for this seems to be related to the relative stability of the two olefins that could be formed in a given elimination reaction.

The two olefins will show different amounts of resonance stabilization of the hyper conjugative type and removal of hydrogen from the more highly branched carbon atom will generally lead to the more highly branched(and more highly hyper conjugated olefin) .

It is important to indicate that in some cases , formation of the least stable or least highly substituted olefins may be favored when the leaving group is bulky or highly electron attracking or when the attracking base it self is bulky.

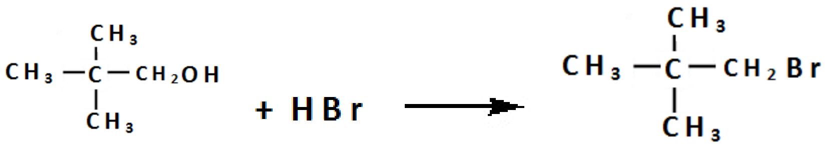
Effects of various factors on the rate of elimination reactions:

1. For organic halides **(R-X)** with a given R group , the rate of **H-X** varies with **X** in the order **I ˃ Br ˃ Cl ˃ F**
2. For a given **X** in series of organic halides **(R-X)** ,the ease of elimination of **HX** follow the order
   Tertiary R ˃ secondary R ˃ primary R
3. In contrast to S_N^2 reaction , E_2 reactions are only slightly influenced by steric hindrance and take place easily with tertiary halides.
4. Elimination reactions are favored over substitution reactions in the presence of strong bases.
   This is why E_2 reactions tends to predominate with strongly basic reagents such as NH_2^- , whereas S_N^2 reactions tend to be favored with weakly basic reagent such as iodide, acetateions.
5. Higher reaction temperatures seem to favor E_1 and E_2 reactions over$S_N^1$and S_N^2 reactions.

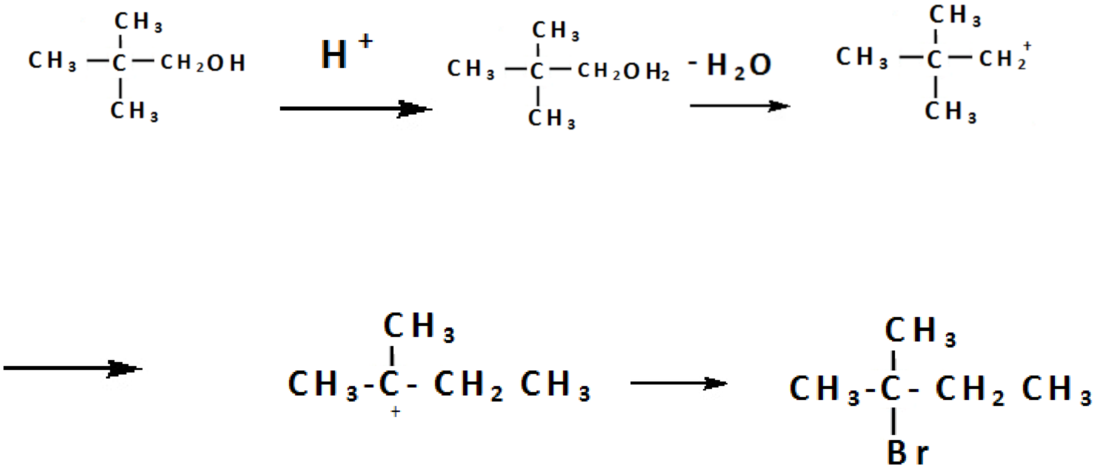
Carbonium ion rearrangement :

In **S_N^1** and **E_2**, the intermediate carbonium ions are known to rearrange if a more stable carbonium ion could be produced.

This property of carbonium ions always complicates the study of displacement reactions. Consider the following example.



Not occur



In the above reaction mechanism, the first step is the usual acid-base reaction of alcohol with aqueous hydrogen bromide.

The second step leads to the carbonium ion which undergoes rearrangement.

In this rearrangement a methyl group migrates with a pair of electrons to the neighboring carbon atom.

This generates a new carbonium ion which on union with bromide ion yields the obtained product, 2-bromo-2-methylbutane.

We assume that the rearrangement take place because the new tertiary carbonium ion (B) is more stable of lower energy than the old primary carbonium ion (A)

This explained previously in terms of hyperconjugation.